DETERMINATION OF THE "NEW" PROBLEM GROUP CHLOROPARAFFINS IN SEDIMENTS BY HRGC-LRMS

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Prof. Dr. Hans-Jakob Wirz

Dekan

All intelligent thoughts have already been thought;

what is necessary is only to try to think them again.

Johann Wolfgang von Goethe (1749-1832)

This work has been carried out in the laboratories of the Institute for Organic Chemistry at the University of Basel in Switzerland under the supervision of Prof. Dr. Michael Oehme.

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LIST OF PUBLICATIONS

Parts of this work are presented in the following publications:

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J. Hüttig and M. Oehme. Presence of chlorinated paraffins in sediments from the North and Baltic Sea. *Archives of Environmental Contamination and Toxicology* (**2005**), 49, 449-457.

J. Hüttig and M. Oehme. Congener group patterns of short and medium chain chloroparaffins in marine sediments. *Organohalogen Compounds* (**2005**), 67, 2041-43.

J. Hüttig and M. Oehme. Characterization of short chain chloroparaffins and consequence for quantification. *Journal of Environmental Monitoring* (**2005**), 7, 319-324.

J. Hüttig, Z. Zencak and M. Oehme. Levels of chlorinated paraffins in North and Baltic Sea sediments. *Organohalogen Compounds* (**2004**), 66, 1321-1326.

TABLE OF CONTENTS

ABBREVIATIONS

CA	Cluster Analysis
CACI-MS	Chloride Attachment Chemical Ion Mass Spectrometry
CH_2Cl_2	Dichloromethane
CH_4	Methane
CID	Collision Induced Dissociation
$C_nH_{2n+2-x}Cl_x$	Sum formula of single chloroparaffins (n = 10-17 and x = 4-10)
Cl	Chlorine content
CP	Chloroparaffin
4,5-DCCD	4,5-Dichlorochlordene
DCM	Dichloromethane
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
d.w.	Dry Weight
EI-MS/MS	Electron Ionization Tandem Mass Spectrometry
ECNI-MS	Electron Capture Negative Ion Mass Spectrometry
GC	Gas Chromatography
HCH	Hexachlorocyclohexane
cis/trans-HEP	*cis/trans*-Heptachlorepoxide
HR	High Resolution
HSQC	Heteronuclear Single Quantum Correlation
i.d.	Internal Diameter
ISTD	Internal Standard
K_{ow}	Octanol water partition coefficient
LOD	Limit of Detection (normally at a signal-to-noise of 3:1)
LOQ	Limit of Quantification (normally at a signal-to-noise of 10:1)
LR	Low Resolution
MC8	Trivial name of chlordane compound
MCCP	Medium Chain Chloroparaffin
MS	Mass Spectrometry
m/z	Mass-to-charge ratio
n.a.	Not analysed
NMR	Nuclear magnetic resonance
OCN	Octachloronaphthaline
PC	Principal Component
PCA	Principal Component Analysis
PCB	Polychlorinated Biphenyl

ABBREVIATIONS

PFTBA	Perfluorotributylamine
Q1 and Q3	Quadrupole 1 and 3
R^2	Coefficient of regression
SCCP	Short Chain Chloroparaffin
SIM	Selected Ion Monitoring
S/N	Signal-to-Noise Ratio
TCN	Tetrachloronaphthalene
TOC	Total Organic Carbon
v/v	Volume/Volume

MEASURING UNITS

cm	centimeter
eV	electron Volt
g	gram
g/mol	gram per mol
L	liter
mm	millimeter
mL	milliliter
ng/g	nanogram per gram
pg/g	picogram per gram
µg	microgram
µL	microliter
µm	micrometer

SUMMARY

Chloroparaffins (CPs) are complex mixtures of *n*-alkanes homologues with variable chain lengths and chlorine contents consisting of several thousands of congeners, homologues, isomers and enantiomers. Although chloroparaffins belong to chemicals of high volume production, little attention has been paid to the analysis and environmental levels of these compounds in the last decades. Short chain chloroparaffins have been included in several regulation programs worldwide since studies demonstrated toxicity to aquatic organisms. However, environmental levels still missing for a detailed risk assessment, especially for aquatic systems.

The aim of the work was to develop a method for the determination of short and medium chain chloroparaffins in sediments. The clean-up should be as simple as possible and the detection carried out by high resolution gas chromatography (HRGC) coupled to low resolution mass spectrometry (LRMS). In total, three mass spectrometric methods were applied for the detection of chloroparaffins in sediments using different ionization techniques (electron ionization (EI), electron capture negative ionization (ECNI) and chloride attachment chemical ionization (CACI)). They allowed to determine short (SCCP) and medium chain CP (MCCP) levels and patterns in sediments from the North and Baltic Sea.

Soxhlet extraction was followed by a clean-up consisting of adsorption chromatography with silica gel and Florisil®, which allowed the separation of CPs from other interfering organochlorines such as polychlorinated biphenyls, toxaphene and DDT-related compounds.

At first, thirty three sediments from the North and Baltic Sea were investigated by EI-MS/MS. Secondly, eight additional sediments from the Seine estuary, Tromsø and Hamburg harbour were analysed as well as fifteen suspended particular matter samples from the rivers Rhine, Neckar, Elbe and from the North Sea. EI-MS/MS allowed simultaneous determination of short, medium and long chain chloroparaffins. Concentrations ranged between 5-355 ng/g dry weight (d.w.) for the North Sea, 45-377 ng/g d.w. for the Baltic Sea, 70-156 ng/g d.w. for the Seine estuary and the harbours of Tromsø and Hamburg as well as 127-669 ng/g d.w. for the samples from Rhine and Neckar.

The application of ECNI-MS and CACI-MS allowed the separate quantification of short and medium chain chloroparaffins and of the homologue and congener group patterns. SCCP concentrations ranged between 8-144 ng/g d.w. and MCCP between 23-407 ng/g d.w. in twenty eight samples (ECNI-MS). The SCCP and MCCP content was determined in those samples exceeding ca. 50 ng/g total CP. Below this level the quantities were too low for this differentiation based on single formular and congener groups. MCCP levels were highest in all samples. Differences in the CP patterns were obtained. Sea sediments were predominated by chlorinated do- and tridecanes and those from rivers, harbours and suspended particular matter samples by chlorinated un- and dodecanes. No difference was observed between the MCCP patterns. Concentrations obtained by CACI-MS were in the range of 13-128 ng/g d.w. for SCCP and between 36-303 ng/g d.w. for MCCP in eighteen sediments from the North and Baltic Sea. The MCCP/SCCP ratios varied between 1.5 and 3.2 and were in good agreement (< 25% relative deviation) with the same sampling location and different years of sample collection. Results obtained by the three methods were in a good agreement with each other (< 34% relative standard deviation).

Furthermore, principal component analysis (PCA) was applied to compare the CP patterns of sediments and suspended particular matter with those of technical mixtures from European producers. Congener and homologue group patterns of marine sediments showed similarities with technical SCCP and MCCP mixtures and differences with those of river sediments and suspended particular matter (ECNI-MS). CP patterns of marine sediments obtained by CACI-MS were similar to technical mixtures with chlorine contents < 50%. Additionally, cluster analysis (CA) was used for the differentiation between technical SCCP and MCCP mixtures. The main criterion of differentiation was the degree of chlorination.

Congener and homologue group patterns of technical SCCP and MCCP mixtures were registered and compared using ECNI-MS and CACI-MS. In contrast to CACI-MS, homologue and congener group patterns obtained by ECNI-MS showed always a shift to the next higher chlorinated congener of the same carbon chain length group. Consequently, the calculated molecular masses and chlorine contents were always higher for ECNI-MS. However, for sediment samples a pronounced shift to congeners with 2-3 more chlorine atoms was observed due to interfering compounds not removed by the clean-up.

Technical CP mixtures and sediments were also characterized by comprehensive two-dimensional (GC×GC) gas chromatography coupled to quadrupole LRMS. For single CP mixtures with the same chlorine content but different carbon chain lengths the same main CP congeners were detected, e.g. congeners with 5-8 chlorine atoms for mixtures with 50% chlorine content. Separation of MCCPs a SCCPs could not be achieved with the selected stationary phase combination of ZB1-ms (first column) and DB-17MS (second column). The applicability of this method was demonstrated for sediments.

The developed clean-up procedure allowed also the determination of chlordane compounds in sea sediments. Detection was carried out by conventional ECNI-MS on two different instruments and by a newly developed method based on electron ionization tandem mass spectrometry (MS/MS). This method showed comparable detection limits in the low pg range except for *cis*-heptachlorepoxide, where detection limits were higher one order of magnitude. Levels of heptachlor, *trans/cis*-chlordane and *trans/cis*–nonachlor were determined. The concentrations ranged between 7-144 pg/g d.w. for *trans*-nonachlor, < 2-29 pg/g d.w. for the *cis* isomer, < 2-135 pg/g d.w. for *trans*-chlordane, < 7-126 pg/g d.w. for *cis*-chlordane and 42-64 pg/g d.w. for heptachlor. *trans*-Nonachlor concentrations were highest in all samples.

1 INTRODUCTION

1.1 Characterization of chloroparaffins (CPs) and chlordanes

Chloroparaffins

Chloroparaffins (CPs, also called polychlorinated *n*-alkanes) are complex mixtures of *n*-alkane homologues with carbon chain lengths between C_{10} and C_{30} and a chlorination degree between 30% and 70%. According to their chain length these mixtures can be divided into short ($C_{10\text{-}13}$, SCCP), medium ($C_{14\text{-}17}$, MCCP) and long chain (> C_{17}, LCCP) CPs. They are further sub-categorized by their weight content of chlorine: < 50%, 50% to 60% and > 60% (Muir *et al.* 2000, Zitko 1980).

Chlordane

Technical chlordane is a complex mixture of more than 140 compounds with six to nine chlorine atoms attached (Dearth and Hites 1991). Commercially available chlordane mixtures primarily contain *cis*- and *trans*-chlordane, *trans*-nonachlor and heptachlor as well as many less abundant chlordanes, chlordenes and nonachlors. The ratio of the *cis*- and *trans*-isomers depends on the manufacturing process (Buchert *et al.* 1989). Figure 1 shows the structure of main chlordane compounds.

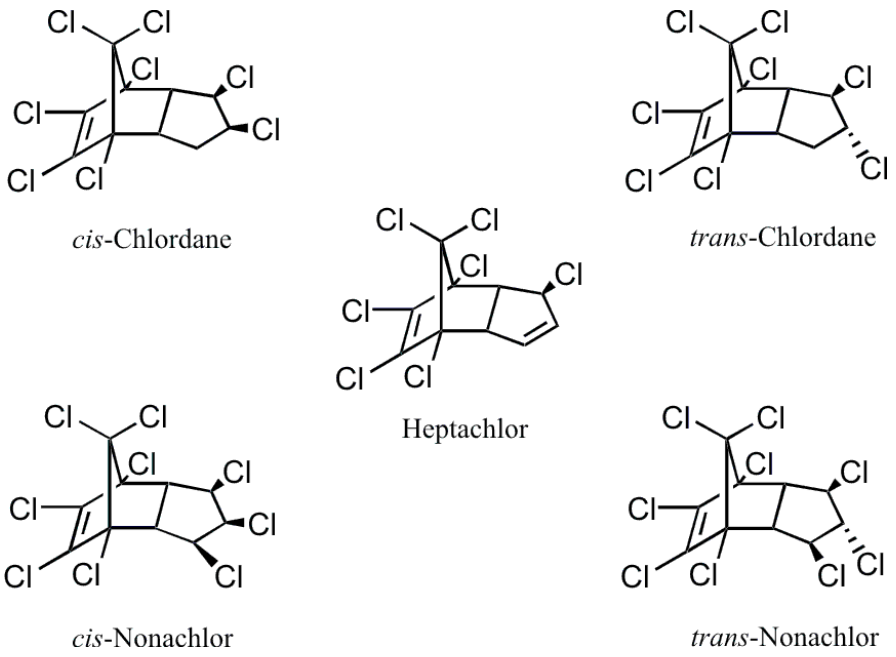

Figure 1. Structure of some important chlordane compounds.

1.1.1 Physical-chemical properties

Chloroparaffins

CPs are colourless to intense yellowish, low to highly oily liquids or glassy to waxy solids boiling over 200 °C with the release of hydrogen chloride. They are insoluble in water but dissolve in most non-polar organic solvents. Their viscosities and densities increase with increasing chlorine content of a given carbon chain length. However, volatility decreases with increasing chain length and degree of chlorination (Drouillard *et al.* 1998). Table 1 summarizes selected physico-chemical properties. SCCPs have similar vapour pressures as other chlorinated organochlorines with the same molecular mass range such as PCBs and toxaphene. The tetra- to hexachlorodecanes can be classified as semi-volatile at ambient temperatures (Muir *et al.* 2000). Drouillard *et al.* (1998) reported Henry's law constants (HLC) in the range of 0.8-15 Pa m^3 mol^{-1} for chlorodecanes and also for lower chlorinated un- and dodecanes (Cl_{5-7}). Low molecular weight CPs may volatilize from water to air in temperate and tropical environments similar to e.g. organochlorine pesticides.

Higher chlorinated MCCPs (> Cl_7) had low estimated Henry's law constants (< 0.34 Pa m^3 mol^{-1}) and HLCs decreased with increasing degree of chlorination (Drouillard *et al.* 1998). On the basis of the log K_{OW} values (octanol-water partition coefficient, in general > 4.4), CPs can be classified as very hydrophobic compounds.

Chlordane

Chlordane is a viscous, light yellow to amber coloured liquid with a melting point of 106-107 °C. The vapour pressure of technical chlordane is 1×10^{-3} Pa at 25 °C and varies between 3.0×10^{-4}-2.9×10^{-3} Pa for *cis*- and *trans*-chlordane for different temperatures (Abadin *et al.* 1994). Its water solubility is poor (32 μg/l) but increases in the presence of humic substances. For pure chlordane a log K_{OW} of 5.54 was estimated and those for single chlordane congeners were between 5.4-6.4 (Karlsson 1998).

Table 1. Vapour pressures [Pa], water solubility [μg/l] and octanol-water partition coefficient (log K_{OW}) of selected chloroparaffin mixtures with different chlorine content [% Cl].

Compound	Chlorine content [% Cl]	Vapour pressure [a] [Pa]	Water solubility [a] [μg/l]	Log K_{OW} [a]
SCCP				
$C_{10\text{-}13}$	49	2.1×10^{-2} at 40 °C 0.7 at 80 °C		4.4-6.9
$C_{10\text{-}13}$	60			4.5-7.4
$C_{10\text{-}13}$	63			5.5-7.3
$C_{10}H_{18}Cl_4$	51		2370	4.8
$C_{10}H_{13}Cl_9$	71		400	5.6
$C_{13}H_{23}Cl_5$	49		78	6.1
$C_{13}H_{16}Cl_{12}$	71		64	7.2
MCCP				
$C_{14\text{-}17}$	45	2.3×10^{-3} at 40 °C 0.16 at 80 °C		5.5-8.2
$C_{14\text{-}17}$	52	$1.3\text{-}2.7\times10^{-4}$ at 20 °C 1.1×10^{-3} at 45 °C 6×10^{-3} at 60 °C 5×10^{-2} at 80 °C		5.5-8.0
C_{15}	52		5	
C_{16}	52		10 (freshwater) 4 (seawater)	
$C_{14}H_{26}Cl_4$	42			7.0
$C_{14}H_{23}Cl_7$	57			6.4
$C_{16}H_{20.6}Cl_{13.4}$	69			7.4
$C_{16}H_{21.7}Cl_{3.3}$	35			7.2
$C_{17}H_{32}Cl_4$	38			8.5
$C_{17}H_{27}Cl_9$	58			7.9
LCCP				
$C_{>20}$		2.7×10^{-4} at 80 °C		
$C_{18}H_{34}Cl_4$	36		2.3×10^{-2}	9.1
$C_{18}H_{30}Cl_8$	53		7.7×10^{-1}	7.9
$C_{20}H_{38}Cl_4$	34		1.2×10^{-3}	10.1
$C_{20}H_{33}Cl_9$	54		9.8×10^{-2}	8.7

[a] Data from European Chemicals Bureau (2002), GDCh Advisory Committee on Existing Chemicals of Environmental Relevance (1992), Sijm and Sinnige (1995), Tomy *et al.* (1998a)

1.1.2 Production and quantities used

Chloroparaffins

CPs are produced by the reaction of different *n*-alkane fractions (either liquid paraffins or dissolved in e.g. carbon tetrachloride) derived from petroleum distillation with molecular chlorine under light. The reaction takes place at temperatures between 50 and 150 °C. Because the alkane feedstock consists of *n*-alkanes with varying carbon chain lengths, the final product contains several thousands of different isomers, diastereomers and enantiomers (Shojania 1999). Therefore, CPs are known as the most complex mixtures in the field of organic contaminants.

The first large scale CP production started in 1932 and the annual production is still in the range of 300`000 tonnes worldwide (Muir *et al.* 2000). It is believed that 50% of the CPs produced worldwide are MCCPs with a chlorine content between 45-52% (World Health Organization 1996). In Europe, the consumption of MCCPs has already exceeded that of SCCPs (70% MCCP and 15% SCCP in 1994, World Health Organization 1996). The use of SCCP within the European Union (EU) has been reduced from 13`000 tonnes to 4`000 tonnes during 1994-1998. The total production was ≤ 15`000 tonnes in 1994 (Helcom 2002) due to restrictions in production and use. The current total MCCP production capacity is in the range 45`000-160`000 tonnes/year in the EU (European Chemicals Bureau 2002). Currently, more than 200 commercial mixtures are in use for a wide range of industrial applications (Alcock *et al.* 1999).

Chlordane

Technical chlordane is produced by chlorination of cyclopentadiene to form hexachlorocyclopentadiene and condensation of the latter with cyclopentadiene. The formed chlordene is further chlorinated to chlordane at high temperature and pressure (Dearth and Hites

1991). Chlordane was first synthesized in 1944. 70`000 tonnes were produced by the Velsicol Corporation between 1946-1988 (Dearth and Hites 1991). The Environmental Protection Agency (US EPA) estimated that around 1`750-2`000 tonnes were distributed in 1986. Due to concerns about the risk of cancer, all use of chlordane in the USA was prohibited in April, 1988. However, Velsicol continued to produce the pesticide for export (Africa, South America). In 1997, Velsicol permanently ceased production. Technical chlordane was not manufactured in Europe and Japan but it was commercially available in Germany and other European countries since the 1950s (World Health Organization 1984). In 1976, the pesticide was removed from the German market.

1.1.3 Applications

Chloroparaffins

CPs are mainly used as extreme pressure and temperature additives in metal working fluids (SCCP, MCCP and LCCP with 50-60% chlorine content), as plasticizer in paints, as additives to adhesives and sealants and as flame retardants in rubber and polymeric materials (Muir *et al.* 2000). MCCPs (usually 50-60% chlorine content) are also used as secondary plasticizers in polyvinyl chloride (PVC) and other plastics (European Chemicals Bureau 2002). Medium chain CPs are replacements for short chain CPs in several applications due to SCCP production restrictions in the last years.

Chlordane

Chlordane has been used for more than 35 years as a broad-spectrum contact insecticide (World Health Organization 1984). It was mainly used for non agricultural applications (e.g. house protection, ornamental lawns). Later, technical chlordane and pure heptachlor were also used as pesticides for the control of insects on various types of agricultural crops and vegetation (corn, citrus, deciduous fruits, nuts, vegetables, Abadin *et al.* 1994).

1.2 Environmental behaviour

Chloroparaffins

CPs are generally considered to be persistent. Hydrolysis, oxidation and photolysis with visible or near ultraviolet radiation are insignificant routes of transformation at ambient temperatures, but degradation is possible by micro-organisms (Madeley and Birtley 1980, Omori *et al.* 1987). The ability of aerobic micro-organisms to degrade a range of CPs depends on previous acclimatisation of the microbes, chain length and degree of chlorination. SCCPs (< 60% Cl) appeared to be rapidly and completely degraded, whereas MCCPs and LCCPs degrade more slowly (Madeley and Birtley 1980). Omori *et al.* (1987) concluded that two or more chlorine atoms reduce the dechlorination rate by bacterial strains in soil.

CPs are hydrophobic compounds and adsorb mainly on suspended solids and sediments in the aquatic environment. Once bound, CPs may not be available for direct uptake by fish and by other aquatic invertebrates. However, they can re-enter the food chain through benthic organisms. The low solubility in water (μg/L range) would predict low mobility, but monitoring data worldwide indicate a widespread CP contamination of water and aquatic organisms (World Health Organization 1996). The log K_{OW} values of > 4 suggest that bioconcentration in aquatic systems is of concern. Reported bioaccumulation factors for fish and mussels were in the range of 7`000-138`000. They were higher for SCCPs than for MCCPs (GDCh Advisory Committee on Existing Chemicals of Environmental Relevance 1992, World Health Organization 1996).

As mentioned before, the estimated or measured Henry's law constants for CPs were similar to those of chlorinated pesticides such as toxaphene, chlordane and aldrin (Sunito *et al.* 1988). Dispersion by the atmosphere was reported from United Kingdom, the Canadian Arctic and in a

background area in the Czech Republic (Figure 2). Air, biota and sediment samples showed similar patterns with mainly lower chlorinated decanes and undecanes (Peters *et al.* 1998, Stejnarova *et al.* 2005, Tomy *et al.* 2000). Measured levels of CPs in remote areas like the Arctic can be seen as evidence for long range transport and deposition (Borgen *et al.* 2000, Tomy *et al.* 1999a). The main SCCP components $C_{10}H_{17\text{-}15}Cl_{5\text{-}7}$, $C_{11}H_{18/17}Cl_{6/7}$ and $C_{12}H_{20/19}Cl_{6/7}$ had estimated atmospheric half-lives greater than two days (UNECE ad hoc Expert Group on POPs 2003). More volatile SCCP compounds were also detected in biota from the Arctic (Tomy *et al.* 2000).

The lowest SCCP and MCCP (air and sediment) concentrations were found in the Arctic and the highest in industrialized areas (Barber *et al.* 2005, Stejnarova *et al.* 2005). But there is a lack of MCCP patterns from different areas worldwide. CP patterns are completely missing for water samples. A comparison of patterns in biota is difficult, since there are a lot of parameters influencing the concentrations of different congener groups (e.g. bioaccumulation, metabolization). Higher bioaccumulation factors were reported for C_{13}-compounds (ca. $> 10^5$) compared to C_{10}-, C_{11}- and C_{12}-compounds (2-4 $\times$ 10^4 for lake trout) as well as for the SCCP mixture (3.6 $\times$ 10^5, UNECE ad hoc Expert Group on POPs 2003).

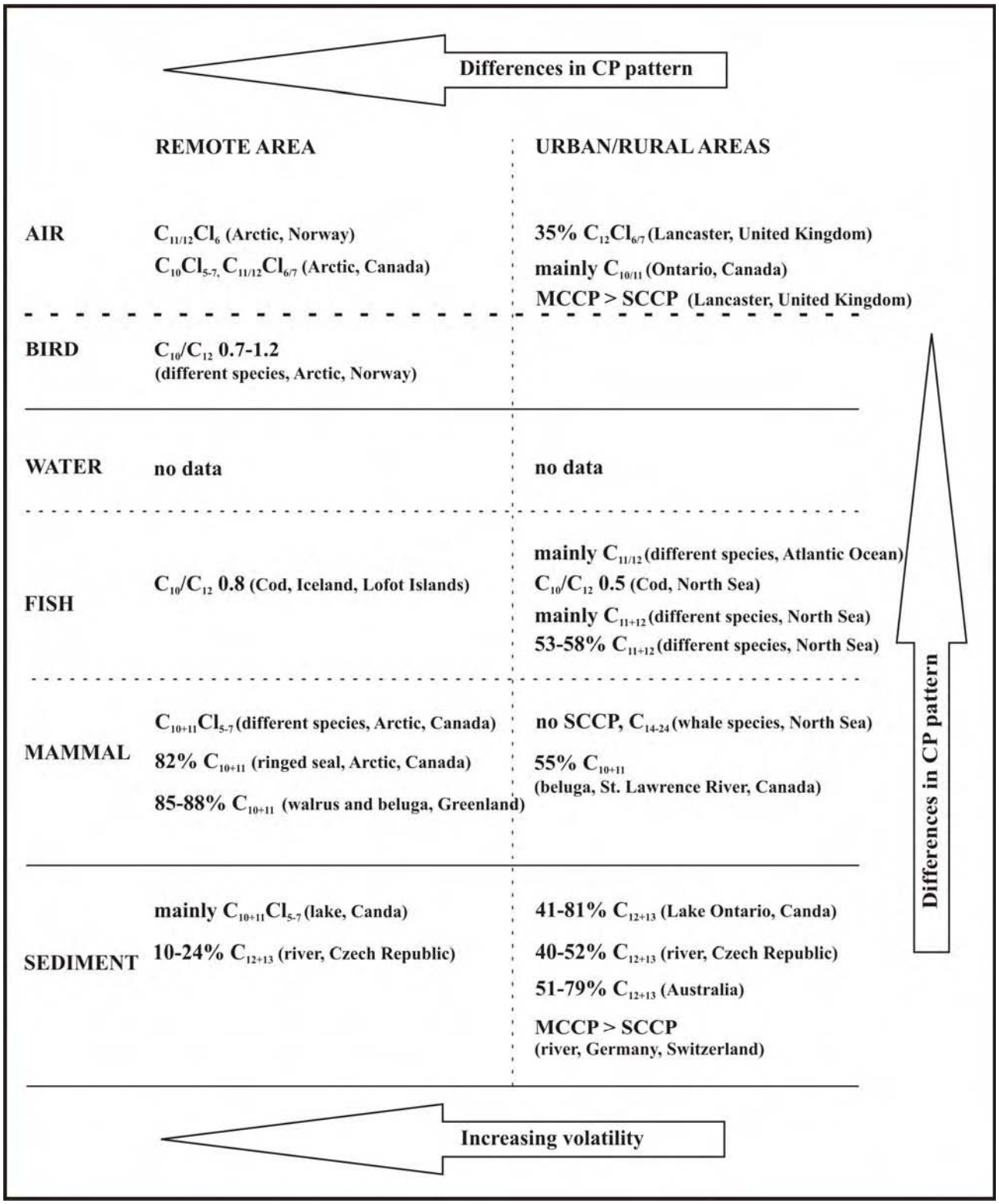

Figure 2. Summary of characteristic CP patterns in sediment, water, air and biota as well as from remote and urban/rural areas (Barber *et al.* 2005, Borgen *et al.* 2000, European Chemicals Bureau 2002, Greenpeace 1995, Kemmlein *et al.* 2002, Lahaniatis 2001, Marvin *et al.* 2003, Peters *et al.* 2000, Reth *et al.* 2005a, Stejnarova *et al.* 2005, Tomy *et al.* 1998a, Tomy *et al.* 2000, UNECE ad hoc Expert Group on POPs 2003).

Chlordane

The intensive use of chlordane led to the accumulation of considerable residues in agriculture land (Abadin *et al.* 1994). Moreover, its relative persistence and sufficient volatility caused an ubiquitous presence in the environment, in food chains and in humans. In contrary to chloroparaffins, abiotic degradation plays an important role for chlordane compounds (Abadin *et al.* 1994). *trans*-Chlordane degrades photochemically more readily than the *cis*-isomer. This is indicated by the change of the *trans/cis*-ratio of chlordane long range transported to the Norwegian Arctic from around 1 in winter to 0.5 in summer (Oehme 1991).

Chlordane in water adsorbs to suspended particular matter and/or sediment, and volatilizes. The mean log K_{OC} (partitioning coefficient between water and particular matter) for *trans*-chlordane is 6.3 (Abadin *et al.* 1994). Water solubility increased with increasing amount of dissolved organic carbon (Johnson-Logan *et al.* 1992). Higher levels of *cis*-chlordane compared to *trans*-chlordane were reported for water samples from the Great Lakes. Chlordane compounds bioconcentrate in marine and fresh water species as well as in bacteria (log $K_{OW} > 5$). Changes in the isomer ratios, the presence of metabolites formed by biodegradation and differences in the congener pattern (different accumulation of selected congeners), were observed in biota (Muir *et al.* 1988).

1.3 Environmental levels

Chloroparaffins

In the past two decades, CP concentrations have been occasionally determined in air, water, sediment, sewage sludge, and biota (Marvin *et al.* 2003, Muir *et al.* 2000, Reth *et al.* 2005a, Stevens *et al.* 2003). CPs were found in industrialized areas as well as in remote regions (Nicholls *et al.*

2001, Stejnarova *et al.* 2005, Tomy *et al.* 1999a). A literature survey showed that even less is known about sediment levels of MCCPs compared to SCCPs in sediments. Table 2 summarises typical CP levels found in sediments worldwide.

Table 2. SCCP and MCCP levels (ng/g dry weight) in sediments worldwide.

Sampling site	Concentration [ng/g d.w.]		Reference
	SCCP	MCCP	
River sediment			
Detroit river	1`800		(Stern and Tomy 2000)
Czech Republic	5-181	18-5`576	(Pribylova *et al.* 2005, Stejnarova *et al.* 2005)
Spain	250-3260		(Parera *et al.* 2004)
Germany	< 5-83	< 10-370	(World Health Organization 1996)
England	300-65`100 [a]	100-10`300	(Nicholls *et al.* 2001)
Japan	5-484 [a]		(Iino *et al.* 2005)
Germany	69-860 [b]		(Maulshagen *et al.* 2003)
Lake sediment			
Lake Ontario, harbour areas	7-290	68	(Stern and Tomy 2000, Tomy and Stern 1999)
Lake Constance	6-10		(World Health Organization 1996)
Lake Zürich		5	(World Health Organization 1996)
Arctic	5		(Tomy *et al.* 1999a)
Sea sediment			
Australia	61-446	1`100-16`400	(Kemmlein *et al.* 2002)

[a] wet weight; [b] suspended particular matter

Kemmlein *et al.* (2002) reported an increased proportion of LCCPs in sediment samples from Australia. LCCPs were often included in CP sum concentrations (C_{10-20} and C_{20-30}) for biota, water and sediment. Therefore, it is not possible to conclude about the amounts of LCCPs present in the environment (World Health Organization 1996).

Chlordane

Technical chlordane was mainly applied in buildings as spray for insect prevention, and therefore detected in air and soil (Offenberg *et al.* 2004). Chlordane was expected to be generally immobile or only slightly mobile in soil. However, its detection in groundwater and sediments indicated the opposite (Abadin *et al.* 1994). Chlordane congeners were also detected in aquatic organisms from polar regions, as well as in human tissue (Abadin *et al.* 1994, Karlsson 1998, World Health Organization 1984). Table 3 gives a survey about levels of chlordane compounds in sediments worldwide.

Table 3. Levels of chlordane compounds [ng/g dry weight] in sediments worldwide.

Location	Concentration [ng/g dry weight]	Reference
Cape Horn, New Zealand	*trans*-Chlordane: < 0.01-0.07	(Simpson *et al.* 1996)
	cis-Chlordane: 0.01-0.07	
	trans-Nonachlor: 0.01-0.07	
	cis-Nonachlor: < 0.01-0.01	
West coast of Korea	0.15-2.4 [a]	(Lee *et al.* 2001)
Mississippi River, USA	Chlordane (*cis*+*trans*): < 0.25-263 [b]	(Rostad 1997)
	Nonachlor (*cis*+*trans*): < 0.25-228 [b]	
Mississippi River, USA	Chlordane: 5-80 [c]	
	Heptachlor: < 0.1-20	
Harbour of Livorno, Italy	*trans*-Chlordane: < 0.1-16.8	(Cicero *et al.* 2001)
	cis-Chlordane: < 0.1-15.6	
Lakes, Canadian Arctic	*trans*-Chlordane: < 0.01-0.70	(Muir *et al.* 1995)
	cis-Chlordane: < 0.01-1.2	
	trans-Nonachlor: < 0.04-0.67	
	cis-Nonachlor: < 0.01-0.66	
	Heptachloroepoxide: < 0.01-0.52 [c]	
Reservoirs in Texas/Giorgia, USA	*trans*-Chlordane: 1-80	(van Metre *et al.* 1997)
Harbour of London, GB	*cis*-Chlordane: 2.1-25	(Fatoki and Awofolu 2003)
	Heptachlor: 1.2	
Mekong River, Vietnam	*trans*-Chlordane: < 0.02-0.14	(Hung *et al.* 2004)
	cis-Chlordane: 0.02-0.11	
	trans-Nonachlor: 0.02-0.34	
Bothnian Bay and Sea, Baltic Sea	*trans*-Chlordane: 0.06-0.12	(Strandberg *et al.* 1998)
	cis-Chlordane: 0.09-0.19	
	trans-Nonachlor: 0.06-0.13	
	cis-Nonachlor: 0.03-0.05	
	cis-Heptachloroepoxide: 0.28-0.34	

[a] sum of *trans-/cis*-chlordane and *trans-/cis*-nonachlor; [b] ng/g organic carbon; [c] no indication

1.4 State of the art in analysis

Chloroparaffins

Most quantitative CP methods are based on gas chromatography (GC) combined with electron capture detection (ECD) as well as high or low resolution mass spectrometry (HRMS or LRMS) (Nicholls *et al.* 2001, Nilsson *et al.* 2001, Tomy *et al.* 1999). Detection of CPs by mass spectrometry often involves electron capture negative ion detection (ECNI) using methane as reagent gas due to its high selectivity and sensitivity (Coelhan 1999, Froescheis and Ballschmiter 1998, Gjos and Gustavsen 1982, Schmid and Müller 1985, Tomy *et al.* 1999b). Other techniques were developed by employing electron ionization (EI) MS or tandem MS (Castells *et al.* 2004, Junk and Meisch 1993, Moore *et al.* 2003, Zencak *et al.* 2003, Zencak *et al.* 2004). Kemmlein *et al.* (2002) reported a HRGC-LRMS method based on the dechlorination of CPs in the injector.

An alternative reagent gas mixture consisting of methane and dichloromethane was applied successfully for the detection of CPs in technical mixtures and environmental samples by negative ion chemical ionisation (Zencak *et al.* 2003). A high degree of fragmentation compared to ECNI-MS was observed, when positive ion chemical ionisation (PICI) MS was used (Castells *et al.* 2004). The use of high-performance liquid chromatography combined with chloride-enhanced atmospheric pressure chemical ionization for the determination of CPs was described as alternative to gas chromatographic methods (Zencak and Oehme 2004).

Recently, GC×GC with electron capture negative ion detection time-of-flight mass spectrometry (ECNI-TOF-MS) was used to study the composition of SCCP, MCCP and LCCP mixtures (Korytar *et al.* 2005b). The applicability of this method was shown for dust samples. Zencak *et al.* (2005) and Castells *et al.* (2004) compared different mass spectrometric methods for the determination of

chloroparaffins. The results of the investigated methods were comparable for the analysis of standards and real samples (fish or sediment) and showed a satisfying accuracy including those based on low resolution MS (LRMS).

Chlordane

The principal method for the determination of chlordane isomers is high resolution gas chromatography in combination with electron capture detection (ECD) or mass spectrometry (Abadin *et al.* 1994). The use of ECNI-MS allows to monitor the molecular ion of chlordane compounds and instrumental detection limits are in the pg range (Dearth and Hites 1991, Karlsson 1998). Co-elutions of *cis*- and *trans*-heptachlorepoxide as well as oxychlordane on relatively non-polar stationary phases can be overcome by the selective ion detection and ECNI-MS (Karlsson 1998). Separation of *cis*- and *trans*-heptachlorepoxide by GC×GC is also possible (Korytar *et al.* 2005a). Chlordanes undergo an intensive fragmentation under electron impact (EI) conditions (Dearth and Hites 1991). Also, HRGC-EI-MS/MS in an ion trap was successfully applied for the determination of *trans*-nonachlor, *cis*- and *trans*-chlordane (Pyle and Marcus 1997). The applicability of positive ion chemical ionization (PICI) in an ion trap was investigated for the detection of chlordane compounds with different non-conventional reagent gases (Zencak *et al.* 2001).

1.5 Problems in CP analysis

1.5.1 Interferences

CP chromatograms normally show a big hump of more or less unresolved peaks. CPs elute over a wide range and co-elute with other halogenated compounds such as toxaphenes, chlordanes and PCBs. Therefore, the analysis of CPs requires an efficient sample clean-up (Parera *et al.* 2004, Reth *et al.* 2005a, Stejnarova *et al.* 2005). Furthermore, ECNI-MS methods based on monitoring of the ubiquitous *m/z* 70-73 ions (Cl_2^- and HCl_2^-) are sensitive to interferences by other organochlorine compounds giving the same fragment ion (Parera *et al.* 2004). If these interferences are not selectively removed during the sample clean-up, they will lead to an overestimation of CPs. Interferences from other chlorinated compounds present in environmental samples could be suppressed by the use of methane/dichloromethane as reagent gas mixture in the NICI mode (Zencak *et al.* 2003). Also, an increased selectivity and sensitivity (detection of lower chlorinated CPs) was possible with this method.

The use of high resolution MS (HRMS, resolution of 12'000) was proposed to achieve a sufficient sensitivity and selectivity to reduce interferences from other polychlorinated compound classes and from CP congeners with the same nominal mass to charge ratio (Tomy *et al.* 1997). ECNI-MS simultaneously forms $[M-Cl]^-$, $[M-HCl]^-$ and $[M+Cl]^-$ ions (Tomy *et al.* 1998b). Therefore, interferences between congeners are possible within SCCP (interference of $[M+Cl]^-$ for $C_{11}H_{18}Cl_6$ and $[M-Cl]^-$ for $C_{11}H_{16}Cl_8$) or between SCCP and MCCP congeners (interference of $[M-Cl]^-$ for $C_{11}H_{17}Cl_7$ and $[M-Cl]^-$ for $C_{16}H_{29}Cl_5$). Nevertheless, the quantification of major congener groups is not affected by any interference (Reth and Oehme 2004). But this is not the case for the quantification of C_{16} and C_{17} congeners in the presence of high levels of C_{11} and C_{12}-CPs. The authors suggested to check the correct ratio of the two most abundant isotopes of the $[M+Cl]^-$ ions,

retention time ranges and HRGC signal shapes (Reth and Oehme 2004). Moreover, the use of CH_4/CH_2Cl_2 as reagent gas led to an enhanced formation of $[M+Cl]^-$ ions and suppressed the formation of $[M-Cl]^-$ ions (Zencak *et al.* 2003).

1.5.2 Differences in response factors

It could be shown that the response factor for different CP mixtures and single compounds varied strongly, when ECNI-MS was employed (Zencak 2004). Congeners with a higher degree of chlorination had higher response factors. Consequently, the selection of the CP quantification standard had a strong influence on the results and could cause systematic errors of up to several hundred percents (Zencak *et al.* 2005).

Other techniques were developed to minimise response factor differences such as electron ionization (EI) tandem MS selecting fragmentations being little influenced by congener composition (Castells *et al.* 2004, Moore *et al.* 2003, Zencak *et al.* 2004). EI-MS/MS allowed the simultaneous, non-specific determination of the sum of short, medium and long chain CP congeners without the determination of congener group pattern. However, the latter is essential to detect congener-specific differences in biota, between sample locations due to transport processes (Marvin *et al.* 2003). The use of methane/dichloromethane mixture as reagent gas for the determination of CPs allowed to overcome the strong variation of response factors (Zencak *et al.* 2003). The relative response factor of single CP compounds varied by a factor of 22.5 for ECNI-MS and decreased to 2.4 by applying a methane/dichloromethane reagent gas mixture.

1.5.3 Quantification

An international interlaboratory study compared quantitative methods for short chain CPs in 1999. Deviations up to several hundred percents were found (Tomy *et al.* 1999b). It could be shown that additional systematic errors were caused by the use of different commercial technical mixtures as quantification standards. It was suggested that interferences by co-eluting congeners were responsible, especially when low resolution mass spectrometry was employed. However, this does not explain why CP standards gave better results with a quite different retention profile and congener composition compared to the investigated sample, than a standard with a more similar composition (deviations between 2-74% compared to - 30 to 310%) (Tomy *et al.* 1999b).

Investigations with several CP mixtures synthezised from pure *n*-alkanes showed that an optimised reference standard has to be selected for each sample (Coelhan *et al.* 2000). The authors suspected not only differences in the *n*-alkane chain composition between sample and standard as reason for systematic deviations, but also deviating distributions of chlorine homologues within one *n*-alkane chain length. Therefore, the authors suggested two procedures to minimise their influence on quantification. First, the abundance ratio of the two ions selected for quantification by MS had to be similar in sample and standard. Second, an individual mixing of reference standards was proposed to obtain a peak pattern similar to that of the sample.

Recently, a new quantification procedure was described which compensates the influence of standard composition and chlorine content on response factors (Reth *et al.* 2005b). A linear correlation was found between the response factor of CPs in a technical mixture and the degree of chlorination. This procedure allowed the calculation of the response factor of CPs present in a sample and the correction of the differences in the chlorination degree of CPs in the sample and in the applied quantification standard.

1.6 Legislation

Chloroparaffins

Studies have demonstrated that SCCPs are toxic to aquatic organisms and bioaccumulate in different species (Tomy *et al.* 1998a). Furthermore, SCCPs are carcinogenic in rats and mice (Farrar 2000). The International Agency for Research on Cancer (IARC) classified SCCPs in group 2B as possibly carcinogenic to humans (World Health Organization 1996). Consequently, several organizations and environmental agencies have imposed regulations on the application and/or environmental release of SCCPs. The majority of the countries joining the "Convention for the Protection of the Marine Environment of the Northeast Atlantic" (OSPAR Convention) voted in favour of a prohibition of SCCP releases to the sea. This decision included the ban of SCCP production and use (Farrar 2000, Helcom 2002). SCCPs were also included in the list of hazardous substances by HELCOM (Helsinki Commission, Baltic Marine Environment Protection Commission). The HELCOM objective is to prevent pollution of the convention area by continuously reducing discharges, emissions and losses of hazardous substances with the aim of achieving concentrations in the marine environment near background for naturally occurring substances and close to zero for man-made chemicals.

In particular, water pollution by SCCPs is of concern. Therefore, the European Union included SCCPs in the list of priority hazardous substances in the water policy directive 2000/60/EC (European Community 2000, European Community 2001). It contains substances, which are persistent, toxic and bioaccumulative in food webs. The Water Framework Directive has the same aim and actionplan as HELCOM. Furthermore, the use of SCCPs has been restricted for the metal-working and leather industry since January 2004. SCCPs were already banned in Germany in 2003 (Umweltbundesamt 2003). The decision is based on the SCCP risk assessment, which concluded that a risk for aquatic organisms exists arising from local emissions of SCCPs from the metal-

working and leather industry (European Commission 1999). Priority is given for MCCP risk assessment under the OSPAR strategy and priority chemicals under the Water Framework Directive (EPA (UK) 2002).

The United States of America do not regulate the use or marketing of SCCPs (UNECE ad hoc Expert Group on POPs 2003). The short chain product (C_{12}) with 58% chlorine content is the only classified and labelled as carcinogenic. However, some suppliers in the USA have decided to label other SCCPs in the same way (Eurochlor 2004). An environmental and human health risk assessment of SCCPs was published in 1993 for Canada (Government of Canada 1993). SCCPs were declared as "toxic" as defined under paragraph 11(c) of the Canadian Environmental Protection Act. To fill up the missing data gaps of this report, an additional report with new and more detailed CP data was published in 2003 by Canadian scientists (UNECE ad hoc Expert Group on POPs 2003).

Some of the reports also included possible alternatives or substitutes of SCCPs (see Table 4). MCCPs are considered to be less toxic and less persistent than SCCPs (Thompson and Comber 2000). However, MCCPs meet some of the POP (Persistent Organic Pollutant) criteria (e.g. vapour pressure, log $K_{OW} > 5$, lack of biodegradation (Lerche *et al.* 2002)).

Table 4. Possible alternatives or substitutes of SCCP (UNECE ad hoc Expert Group on POPs 2003).

Use	Possible Alternative to SCCP
Extreme pressure additives in metal working fluids	MCCPs, LCCPs, alkyl phosphate esters sulfonated fatty acid esters
Plasticizers in paints	MCCPs
Additives in sealants	MCCPs, LCCPs, phthalate esters
Leather industry	LCCPs, natural animal and vegetable oils
Paints, coatings	LCCPs, phthalate esters, polyacrylic esters
Rubber	LCCPs

Chlordane

Chlordane use was regulated in 1979 in the US with restrictions on agriculture uses (Offenberg *et al.* 2004). After July 1983, the use of chlordane was only allowed for underground termite control in houses. However, all commercial use of chlordane has been strictly prohibited in the US in 1988. The pesticide was removed from the German market in 1976.

Chlordane and heptachlor belong to the so-called "dirty dozen", a group of twelve classes of persistent organic pollutants (POPs) including aldrin, chlordane, dichlorodiphenyl-trichloroethane (DDT), dieldrin, endrin, heptachlor, hexachlorbenzene, mirex, polychlorinated biphenyls (PCB), polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans as well as toxaphene (Ballschmiter *et al.* 2002). The ban of those twelve POPs was signed in 2001 (Stockholm Convention).

1.7 Persistent organic pollutant (POP) classification

Persistent organic pollutants are defined as substances which are persistent, toxic, able to bio-accumulate and which undergo long-range air transport into remote areas. The verification of all four criteria nominates a substance as a POP candidate. Additionally, a positive result of an internationally agreed risk assessment is necessary to consider a POP candidate definitely as a POP. Members of the United Nations Economic Commission for Europe (UN-ECE) signed a legally binding protocol on POPs in 1998 under the Convention of Long-Range Transboundary Air Pollution (LRTAP POP Protocol).

In 2001, a treaty was formally signed in Stockholm, which intends to control the production, import, export, disposal and use of toxic chemicals that persist for decades in the environment.

After ratification by at least 50 countries, the treaty has become international law in 2005. Compared to the LRTAP POP protocol the 2001 treaty included only 12 instead of 16 substances or substance classes (Ballschmiter *et al.* 2002). The LRTAP POP protocol defined criteria how compounds can be added further to the list of persistent compounds. Table 5 lists these criteria and shows values for chlordane as already included on this list and for SCCPs as a potentially new POP candidate. SCCPs fulfil the POP criteria but there is still a lack of data for persistence, toxicity and environmental levels. Partly, the published data were contradictory.

Table 5. POP criteria and values of chlordane and SCCPs.

Property	Criteria [a]	"Old" POP member chlordane	"New" POP candidate SCCP
Long range transport	Half life in air (> 2 days)	8 days (predicted)	1.9-7.2
	Vapour pressure (< 1000 Pa)	0.001 Pa	0.02
	Present in remote regions (e.g. Arctic)	yes	yes
Persistence	Half life in water (> 60 days)	7.6 years	60 days (marine)
	soil (> 180 days)	> 20 years	no data
	sediment (> 180 days)	no data	> 180 days
Bioaccumulation/ Bioconcentration	BCF > 5`000 (fish)	7`100-37`800	> 5`000 for fish and mussel
	Log K_{OW} > 5	6.0	4.4-7.4
	Molecular weight < 700	yes	yes
Toxicity potential	Humans	potential carcinogen	possible carcinogen
	Organisms	acute toxic to rats	chronic toxicity to aquatic organisms

[a] Criteria from (Ballschmiter *et al.* 2002)

2 AIM OF THE WORK

The aim of this work was to establish methods for the quantitative analysis of chloroparaffins (CPs) and chlordanes in sediments. The methodology is based on gas chromatography (GC) coupled to mass spectrometry (MS) with different ionization techniques. Chlordanes, short and medium chain chloroparaffins as well as CP congener and homologue group patterns were determined in sediments from the North and Baltic Sea since data from these regions are completely missing. In addition, the following problems and applications were studied.

River sediment samples and suspended particular matter samples from Europe were also analyzed to establish CP data for comparison with the North and Baltic Sea.

A significant advance in chromatographic separations was made with the introduction of comprehensive two-dimensional gas chromatography. Therefore, separation of technical short and medium chain chloroparaffin mixtures by two-dimensional GC electron-capture negative ionisation quadrupole mass spectrometery was evaluated. One main goal was to achieve the separation of short and medium chain chloroparaffins. The applicability of this approach was demonstrated for sediment extracts.

So far, technical CP mixtures applied for quantification were only characterized by their carbon chain lengths and chlorine content. Chemometric methods such as cluster analysis and principal component analysis were evaluated as tools to characterize mixtures from different European producers.

Finally, the comparability of chlordane results obtained by two different mass spectrometers in combination with two different ionization techniques was investigated. A goal was to explore if electron ionization combined with mass spectrometry can be used for chlordane analysis and if this technique can overcome problems such as co-elution by other chlordanes.

3 EXPERIMENTAL

3.1 Chemicals and solvents

SCCP (C_{10-13}, 51.5, 55.5 and 63.0% Cl content) and MCCP ($C_{14-17,}$ 47.0, 52.0 and 57.0% Cl content) technical mixtures as solutions in cyclohexane (concentration 100 ng/µL) were purchased from Ehrenstorfer (Augsburg, Germany). $^{13}C_{10}$-*trans*-chlordane (Cambridge Isotope Laboratories, Andover MA) was used as an internal standard (1 ng/µL), and hexachlorocyclohexane, dissolved in cyclohexane (HCH, Ehrenstorfer, Germany) was employed as recovery standard at concentrations of 1 ng/µL. Hordalub 17, 80 and 500 were from Hoechst, Germany and Cereclor™ 60L and 70L from ICI, England. The MCCP mixtures Hordaflex SP, Hordalub 80 EM, Chlorparaffin 40fl and 45fl were manufactured by Hoechst, Germany, and Cloparin 50 by Caffaro, Italy and Cereclor™ S52 by ICI, England. All were dissolved in cyclohexane at concentrations of 7.5 ng/µL. Single CP homologues (C_{10}, C_{11}, C_{12}, C_{13} with chlorine contents between 50-70%) were provided by Dr. Mehmet Coelhan from the Technical University of Munich and diluted in cyclohexane to concentrations of 100 ng/µL.

Cis/*trans*-chlordane, heptachlor and *cis*/*trans*-nonachlor were purchased from Promochem (Poland) and dissolved in cyclohexane (2.28, 2.6, 11.34, 1.79 and 2.29 ng/µL). Oxychlordane and *cis*/*trans*-heptachlorepoxide were available as solutions in cyclohexane (10 ng/µL) from Ehrenstorfer (Germany). Octachloronapthaline (OCN) and 1,2,3,4-tetrachloronaphthaline (TCN, Ehrenstorfer, Germany, 10 ng/µL in cyclohexane) as well as MC8 and 4,5-dichlorochlordene (4,5-DCCD) were evaluated as internal standards. MC8 was isolated from technical chlordane by Karlsson (1998), and 4,5-DCCD was synthesized by Karlsson *et al.* (1997). Both substances were dissolved in

cyclohexane at concentrations of 1 ng/µl. PCB 153 (180 pg/µL), Toxaphene #44 (10 ng/µL) and p,p´-DDT (265 ng/µL) were used as model compounds to test the selectivity of the clean-up. All standard solutions were diluted further when needed.

All solvents were of pesticide residue grade and obtained from Scharlau (Barcelona, Spain). Florisil® (60-100 mesh) and sodium sulphate (Pestanal®) were purchased from Fluka (Buchs, Switzerland), and silica gel from Merck (0.04-0.063 mm, Darmstadt, Germany).

3.2 Sediment samples and suspended particular matter (SPM)

3.2.1 Sampling and storage of sediments

Sediment samples were collected from the North and Baltic Sea (for sites see Table 6) by the Federal Maritime and Hydrographic Agency (Hamburg, Germany) in August/September 2001/2002 and May/June 2003/2004. Sampling was performed using a grab sampler (surface slice, 0-2 cm). Sediments were frozen immediately after sampling in aluminium boxes until analysis (-24 °C). Total organic carbon (TOC) content was determined by the Federal Maritime and Hydrographic Agency (Vario EL from Elementar, Germany).

Further sediments from the Seine estuary, Tromsø harbour and Hamburg harbour as well as suspended matter from Rhine and Neckar (for sites see Table 7) were obtained from the following institutions:

1. Laboratoire d`Etudes ed d`Analyses, Le Havre, France ;
2. Akvaplan-niva, Tromsø, Norway;

3. Behörde für Wirtschaft und Arbeit, Hamburg, Germany;

4. Landesanstalt für Umweltschutz, Karlsruhe, Germany.

Suspended particulate matter (SPM) was freeze-dried by the Landesanstalt für Umweltschutz, Karlsruhe, Germany, and the fresh sediment samples from Hamburg harbour and the Seine estuary were handled in the same way as samples from the North and Baltic Sea. TOC in sediments from Rhine and Neckar were determined by the Landesanstalt für Umweltschutz, Karlsruhe, Germany and in all other samples by the Department of Geography, University of Basel, Switzerland.

Table 6. Description of sediments including sample name, sampling site, year of sampling and total organic carbon (TOC) content [%]. The HRGC-LRMS methods applied for CP analysis and determination of the CP formular group patterns (X) are indicated.

Sample	Location	Year of sampling	TOC [%]	EI-MS/MS	ECNI[a]-MS	CACI-MS
Baltic Sea						
710	54°25.10´N/10°13.30´E	2001	3.10	X		X
		2002	5.28	X		X
		2004	0.48	X	X	X
715	54°03.00´N/10°50.90´E	2001	2.90	X		X
		2004	3.08	X	X	X
718	54°19.00´N/11°33.00´E	2001	3.80	X		X
		2004	3.64	X	X	X
721	55°00.00´N/14°05.00´E	2001	6.00	X		X
		2002	5.18	X		X
		2004	4.86	X	X	X
ECKFBU	54°28.00´N/9°52.00´E	2004	4.00	X	X	X
ODER	54°08.00´N/14°10.00´E	2004	0.09	X	X	X
RUDEN	54°11.20´N/13°46.00´E	2004	2.81	X	X	X
North Sea						
KS 8	54°02.00´N/8°12.50´E	2002	0.34	X		
		2003	0.82	X	X	X
		2004	1.21	X	X	X
KS 11	54°04.00´N/8°07.50´E	2002	1.67	X		X
		2003	1.10	X	X	X
		2004	2.50	X	X	X
BL 2	54°14.00´N/8°22.50´E	2002	0.57	X		
BL 4	54°30.00´N/7°48.00´E	2002	0.21	X		
UE 18	54°30.00´N/7°60.00´E	2002	< 0.1	X		
UE 28	54°45.00´N/8°12.00´E	2002	0.1	X		
ES 1	53°40.50´N/6°30.00´E	2003	0.06	X		
Ti 13	54°22.50´N/7°38.70´E	2003	0.07	X		
UE 15	54°30.00´N/6°30.00´E	2003	0.23	X		
SSL	54°54.90´N/8°10.10´E	2003	2.77	X		
UE 20	55°00.00´N/6°30.00´E	2003	0.37	X		
L1	55°03.00´N/8°12.00´E	2003	0.13	X		
WB 5	55°04.00´N/6°20.00´E	2003	0.46	X		
UE 67	55°15.00´N/4°30.00´E	2003	0.12	X		
UE 70	55°45.00´N/4°00.00´E	2003	0.07	X		
WB 1	55°50.00´N/6°35.00´E	2003	0.03	X		
			Sum	**33**	**11**	**18**

[a] Triple quadrupole 1200L (Varian, Walnut Creek, USA)

Table 7. Analysed samples of river sediments and suspended particular matter (SPM) including sample name, sampling site, date of sampling and total organic carbon (TOC) content [%]. The HRGC-LRMS methods applied for CP analysis and determination of the formular group patterns (X) are indicated.

Sample	Location and date of sampling	TOC [%]	EI-MS/MS	ECNI-MS[a]
Sediment				
Seine estuary 1	49°27.1´N/0°1.13´E (March 2004)	1.6	X	X
Seine estuary 2	49°27.6´N/0°3.3´E (March 2004)	0.1	X	X
Seine estuary 3	49°28.0´N/0°38.4´E (March 2004)	0.8	X	X
Hamburg 1	Hamburg harbour (December 2003)	3.1	X	X
Hamburg 2	Hamburg harbour (February 2004)	3.0	X	X
Hamburg 3	Hamburg harbour (December 2003)	2.2	X	X
Tromsø 1	69°38.6´N/18°57.1´E (October 2002)	1.8	X	X
Tromsø 2	69°38.6´N/18°57.0´E (October 2002)	2.4	X	X
Suspended particular matter				
Elbe	Elbe (August 2002)	7.9	X	X
North Sea 1	51°30.0´N/2°40.0´E - 50°0.0´N/2°0.0´E (July 2002)	5.7	X	n.a.
North Sea 2	54°9.8´N/6°20.9´E (August 2002)	10.7	X	n.a.
Neckar 1	Km 8, 5. August 2002	5.7	X	X
	2. September 2002	3.6	X	X
	25. November 2002	5.9	X	X
	16. December 2003	5.0	X	X
Neckar 2	Km 165, 7. August 2002	3.4	X	X
	5. September 2002	3.2	X	X
	27. November 2002	7.0	X	X[b]
	18. December 2003	6.4	X	X[b]
Rhine	Km 334, 3. August 2002	5.2	X	X
	4. September 2002	1.9	X	X
	18. December 2003	4.4	X	X
		Sum	**22**	**20**

[a] Triple quadrupole 1200L (Varian, Walnut Creek, USA); [b] no addition of ISTD, quantification by ISTD not possible; n.a. not analyzed

Chlordane analysis of marine samples was carried out by HRGC-ECNI-LRMS (HP 5989B). Additionally, chlordane concentrations obtained by ECNI-MS on two instruments and by EI-MS/MS were compared for North and Baltic Sea sediments from 2003-2004 (eleven samples).

3.2.2 Clean-up of sediments

Sediments were dried at room temperature for 10 days (open-air dried in the lab) and sieved with 2 mm mesh size. Normally, 5-10 g sediment was selected (for North Sea sediments with a TOC close to the LOQ up to 50 g), and 10 µL of a solution with $^{13}C_{10}$-*trans*-chlordane and OCN in cyclohexane (concentration 1 ng/µL each) was added as internal standard.

Soxhlet extraction was carried out with 200 ml of *n*-hexane/dichloromethane (CH_2Cl_2, 1:1, v/v) overnight (glass fibre thimbles 603G, Schleicher & Schuell, Dassel, Germany). Elemental sulphur was removed by activated copper powder (230 mesh, Merck, Germany; activated with concentrated nitric acid) during Soxhlet extraction. The extract was concentrated to 1 mL using a Turbovap evaporation system (Zymark, Hutchinson, USA), and subsequently purified by column chromatography containing 1 g of anhydrous sodium sulphate, 16 g of Florisil® (1.5% water (w/w)) and 1 g of sodium sulphate (glass column 20 cm long, 1.5 cm i.d.). Conditioning of the column was carried out with 40 mL of *n*-hexane. Fraction 1 was eluted consecutively with 60 mL of *n*-hexane and 5 mL of dichloromethane, and fraction 2 with 55 mL of CH_2Cl_2. The latter contained the CPs. 10 ng of ε-HCH in 10 µL cyclohexane was added as recovery standard and the extract concentrated to 200 µL by a Turbovap evaporation system prior to analysis.

For sediments from the Baltic Sea and for two from the North Sea (KS8 and KS11) an additional clean-up step was necessary. Sample matrix not persistent to sulphuric acid was removed prior to the Florisil® clean-up by a column containing 1 g of water free sodium sulphate, 20 g of silica gel/sulfuric acid (44%) and 1 g of sodium sulphate (glass column 20 cm long, 2.0 cm i.d.). The extract was concentrated to 1 mL and placed on top of the column. The CP fraction was eluted with

70 mL of *n*-hexane/CH_2Cl_2 (1+1, v/v). The clean-up of the fresh water sediments and suspended matter followed the same procedure.

3.2.3 Separation and quantification

Tables 6 and 7 show the HRGC-MS methods applied for the CP analysis. All samples were analyzed by the following procedure:

Chloroparaffins

- First, all samples were analyzed by EI-MS/MS to obtain the total CP amount (screening). EI-MS/MS had the lowest detection limits (for further details see chapter Results and Discussion).
- Samples with a total CP amount > 50 ng/g dry weight were further characterized by CACI-MS and ECNI-MS to obtain the CP pattern and to determine the SCCP and MCCP concentrations. The analysis by ECNI-MS on a new instrument (Varian 1200L) was only possible for sediment samples from 2003 and 2004 as well as for river sediments and suspended particular matter.
- Selected sediments (2003-2004) were analyzed by both ECNI- and CACI-MS for comparison. Furthermore, two different quantification methods for ECNI-MS were applied (for details see chapter Results and Discussion).

Chlordane

- Analysis of chlordane compounds (*cis/trans*-chlordane and –nonachlor) in marine sediments was carried out by ECNI-MS (HP 5989B) according to a method published by Karlsson (1998).

- Eleven sediments from 2003-2004 were also analyzed by the same ECNI-MS technique on a second instrument.
- A new method based on EI-MS/MS was developed for main chlordane compounds and compared to the results obtained by ECNI-MS on two different instruments.

3.3 Quality Assurance

The following measures were taken to avoid background contamination and CP background. Sediment samples were kept in aluminium boxes in the freezer. Sodium sulphate, Florisil® and silica gel were heated to 600 °C for 24 h. Glassware was soaked in a water bath overnight (20% Deconex® per L, VWR, Switzerland), rinsed with deionised water and heated to 450 °C overnight in a furnace (FE 110H SEV from Rohde, Prutting, Germany). Glass fibre thimbles were heated to 500 °C prior to use. New batches of solvents were analyzed for SCCP and MCCP background. In general, levels of CPs were below the limit of detection in solvents (see chapter Results and Discussion) and in the method blank (calcinated sand heated to 600 °C).

3.4 Instrumentation

All gas chromatographs were equipped with a fused silica capillary column (15 m length, 0.25 mm i.d.) coated with a 0.25 µm film of crosslinked 5% phenylmethylpolysiloxane phase (DB5-MS, J&W Scientific, Folsom, USA). A **HP 5890II gas chromatograph** (Hewlett Packard, Palo Alto, USA) was coupled to a **HP 5989B mass spectrometer** (Hewlett Packard, Palo Alto, USA). It was used for determination of the CP congener pattern in technical CP mixtures and sediments as well as for chlordane analysis of sediments (ECNI- and CACI-MS). Furthermore, a combination of a

CP-3800 gas chromatograph (Varian, Walnut Creek, USA) and a **triple quadrupole mass spectrometer** (1200L, Varian, Walnut Creek, USA) was employed in the ECNI and EI-MS/MS mode for the analysis of CPs and chlordanes in sediments. The GC×GC system was built from a **Trace GC×GC** (Thermo Electron Cooperation, Milano, Italy) equipped with a dual Jet CO_2 modulator and was coupled to a fast scanning **Trace DSQ mass spectrometer** (Thermo Electron Cooperation, Austin, USA). It was used for the CP characterization of technical mixtures and for selected sediments.

Combination of HP 5890II and HP 5989B

Gas chromatographic separations were performed on a HP 5890II gas chromatograph equipped with a split/splitless injector. Splitless injections (2 min) of 1.5 µL volume were carried out at an injector temperature of 275 °C for CPs and of 240 °C for chlordanes. Helium (99.999%, Carbagas, Basel, Switzerland) was used as carrier gas at a column inlet pressure of 68.9 kPa (10 psi). The temperature program for CPs was (determination of recoveries during method validation): 100 °C, isothermal for 2 min, then 10 °C/min to 260 °C, isothermal for 10 min for MCCPs and 5 min for SCCPs (ECNI and CACI) and for chlordanes: 90 °C, isothermal for 2 min, then 30 °C/min to 150 °C, then 4 °C/min to 250 °C and isothermal for 2 min.

A HP 5989B mass spectrometer was employed in the ECNI mode using methane as reagent gas (99.995%, Carbagas, Basel, Switzerland) at a pressure of 1.0-1.6 mbar (0.8-1.2 Torr). The ion source temperature was 200 °C, the quadrupole temperature 100 °C and the transfer line temperature 280 °C for CPs or 250 °C for chlordanes. The electron energy was 100 eV. The mass spectrometer was tuned for optimal performance using perfluorotributylamine (PFTBA) fragments at *m/z* 282, 414 and 452. SCCPs and MCCPs with 5-10 chlorine atoms were detected in the selected ion monitoring (SIM) mode selecting the most abundant isotope ion of the $[M\text{-}Cl]^-$ cluster of each

CP compound (dwell time 75 ms per ion) and *m/z* 419.8 for the internal standard $^{13}C_{10}$-*trans*-chlordane (Reth and Oehme 2004). The mass spectrometric parameters for quantification of chlordanes and of model compounds in the SIM mode are given in Table 8. The dwell time was always 75 ms per ion. Ions for chlordane quantification were divided into two groups. Group II started at 12.55 min and consisted of those for *trans*/*cis*-chlordane, *trans*/*cis*-nonachlor, OCN, MC8 and ISTD. Oxychlordane, heptachlor, *trans*/*cis*-HEP, 4,5-DCCD and HCH were selected for the first group.

Table 8. Ions selected for quantitative analysis of chlordanes, the internal standards (ISTD), the recovery standard (RS) and model compounds to test clean-up efficiency by ECNI-MS (Karlsson 1998).

Substance	Ion	*m/z*	m/z of the most abundant isotope
cis/*trans*-Chlordane	$[M]^-$	406	410
cis/*trans*-Nonachlor	$[M]^-$	440	444
Heptachlor	$[M-2Cl]^-$	300	302
cis-HEP	$[M]^-$	386	388
trans-HEP	$[M-HCl]^-$	350	352
Oxychlordane	$[M-2Cl]^-$	350	352
MC8 (ISTD)	$[M]^-$	406	410
$^{13}C_{10}$-*trans*-Chlordane (ISTD)	$[M]^-$	416	420
OCN (ISTD)	$[M-2Cl]^-$	332	334
TCN (ISTD)	$[M]^-$	264	266
4,5-DCCD (ISTD)	$[M]^-$	302	300
p,p'-DDT	$[M+H-3Cl]^-$	248	248
PCB 153	$[M]^-$	358	360
Toxaphene #44	$[M-Cl]^-$	373	377
ε-HCH (RS)	$[M-Cl]^-$	253	255

CH_2Cl_2 (Scharlau, Barcelona, Spain) employed for CACI-MS was introduced through a modified transfer line by adding a T-piece and a small glass bulb of 6 mL volume filled with dichloromethane (Zencak 2004). A needle valve was used to control the dichloromethane pressure. CACI-MS was performed at a total reagent gas pressure of 2.0 mbar (1.5 Torr) measured at the

transfer line inlet and a CH_4/CH_2Cl_2 pressure ratio of 4:1. SCCPs and MCCPs with 4-10 chlorine atoms were detected in the selected ion monitoring (SIM) mode using the most abundant isotope ion $[M+Cl]^-$ combinations of each CP compound (dwell time 75 ms per ion) and *m/z* 419.8 for the internal standard $^{13}C_{10}$-*trans*-chlordane.

Combination of CP-3800 and triple quadrupole mass spectrometer (1200L)

Gas chromatographic separations were performed on a CP-3800 gas chromatograph equipped with a split/splitless injector. Splitless injections (3 min) of 2.0 µL volume were carried out at an injector temperature of 275 °C for CPs and 240 °C for chlordanes (Combi Pal autosampler, CTC Analytics, Zwingen, Switzerland). Helium was used as carrier gas at a constant pressure of 68.9 kPa (10 psi) or constant flow of 2 ml/min for EI-MS/MS. For ECNI the temperature program was as follow for CPs: 100 °C, isothermal for 2 min, then 10 °C/min to 260 °C, isothermal for 10 min for MCCP and 7 min for SCCP. For chlordanes the temperature program was: 90 °C, isothermal for 2 min, 30 °C/min to 150 °C, 4 °C/min to 210 °C, then 20 °C/min to 260 °C and isothermal for 5 min. For EI-MS/MS the following temperature programs were applied: 100 °C, isothermal for 1 min, then 50 °C/min to 300 °C and isothermal for 3 min (CPs) and 90 °C, isothermal for 2 min, then 15 °C/min to 260 °C and isothermal for 2 min (chlordanes).

A triple quadrupole mass spectrometer was employed in the ECNI mode with methane as reagent gas at an ion source pressure of 7.3 mbar (5.5 Torr). The transfer line temperature was set 280 °C for CPs or 250 °C for chlordanes, the ion source temperature to 200 °C and the manifold temperature at 40 °C. Spectra (SIM mode) were recorded at 70 eV and a filament current of 150 µA. The mass spectrometer was tuned for optimal performance using PFTBA in the auto tune mode for both quadrupoles. SCCPs and MCCPs with 5-10 chlorine atoms were detected in the selected

ion monitoring mode using the two most abundant isotopes of the $[M\text{-}Cl]^-$ cluster for each CP compound (cycle time 0.250 s) and *m/z* 419.8 for the internal standard. Chlordanes were divided in two groups. Group I started at 5 min and consisted of ions for ε-HCH, heptachlor, oxychlordane and *cis/trans*-HEP, which were monitored with a dwell time of 35 ms per ion. Group II started at 12 min and included the ions for *cis/trans*-chlordane, *cis/trans*-Nonachlor, ISTD and OCN.

Parameters for EI-MS/MS were in brief: Transfer line temperature 280 °C for CPs and 250 °C for chlordanes, manifold temperature 40 °C (Zencak *et al.* 2004). EI-MS/MS spectra were recorded at 70 eV (emission current 150-300 μA, dwell time 40 ms for CPs and 50 ms for chlordanes, resolution of Q1 at 0.8 u and of Q3 at 1.2 u and argon as collision gas at a pressure of 0.12-0.15 Pa. CP quantification was based on the collision induced dissociations (CID) *m/z* 91$[C_7H_7]^+ \rightarrow$ 53 $[C_4H_5]^+$, *m/z* 102 $[C_5H_5Cl]^+ \rightarrow$ 65 $[C_5H_5]^+$ and *m/z* 102 $[C_5H_5Cl]^+ \rightarrow$ 67 $[C_5H_7]^+$ (collision energy -10.0 V, -16.0 V and -10.0 V). The precursor ion *m/z* 383 $[M\text{-}Cl]^+$ and the product ion *m/z* 276 $[M\text{-}4Cl]^+$ were chosen for $^{13}C_{10}$-*trans*-chlordane (collision energy -26.0 V). Triple quadrupole parameters for chlordane compounds are given in Table 9. The ions were divided into two groups (group II at 9.35 min).

Table 9. Triple quadrupol parameters for selected chlordane fragment ions and internal standards (ISTD).

Substance	Presursor ion (*m/z*)	Product ion (*m/z*)	Collision energie (V)
Group I (5-9.34 min)			
4,5-DCCD (ISTD)	272	237	-22.5
trans-HEP	217	181	-22.5
Heptachlor	272	237	-22.5
cis-HEP	353	265	-25.0
Oxychlordane	185	121	-17.5
Group II (9.35-15.33 min)			
$^{13}C_{10}$-*trans*-Chlordane (ISTD)	383 $[M\text{-}Cl]^+$	276 $[M\text{-}4Cl]^+$	-26.0
trans/*cis*-Chlordane	373 $[M\text{-}Cl]^+$	266 $[M\text{-}4Cl]^+$	-25.0
trans/*cis*-Nonachlor	409 $[M\text{-}Cl]^+$	300 $[M\text{-}4Cl]^+$	-25.0

Combination of Trace GC×GC and Trace DSQ

Gas chromatographic separations were performed on a Trace GC×GC gas chromatograph with a ZB-1ms column (30 m length, 0.25 mm i.d. and coated with 0.25 µm film of 100% dimethylpolysiloxane, Phenomenex, USA) as first-dimension column. A DB-17MS column (1 m, 0.18 mm i.d. and coated with 0.18 µm of 50% phenylmethylpolysiloxane, J&W, USA) was used as a second column. Press fits were used for the connection. Splitless injections (1 min) of 1.0-2.0 µL volume were carried out at an injector temperature of 280 °C (TriPlus autosampler, Thermo Electron Cooperation, Milano, Italy). Helium (99.999%, PanGas, Dagmersellen, Switzerland) was used as carrier gas at a constant flow of 1.8 ml/min. The temperature program was: 90 °C, isothermal for 1 min, then 30 °C/min to 170 °C, then 4 °C/min to 300 °C for technical CP mixtures and with 2.5 °C/min to 300 °C for sediment samples. Modulation was performed with carbon dioxide (PanGas, Dagmersellen, Switzerland) at the beginning of the second column with a modulation period of 8 s.

A Trace DSQ mass spectrometer was employed in the ECNI mode with methane (99.995%, PanGas, Dagmersellen, Switzerland) as reagent gas with a constant flow of 1 ml/min. The ion

source temperature was set to 180 °C and the transfer line temperature to 290 °C. The electron energy was 120 eV. The mass spectrometer was tuned for optimal performance using PFTBA in the auto tune mode. SCCPs and MCCPs (technical mixtures) were detected in the scan mode (80 ms scan time, scan rate of 11'111 amu/s and mass range of *m/z* 230-600). CPs in sediment samples were also detected in the scan mode (scan time 50 ms, scan rate 5000 amu/s) but with different scan events (7.1 min: *m/z* 230-350, 13 min: *m/z* 300-500, 23 min: *m/z* 350-550 and 33 min: *m/z* 400-600).

3.5 Structure elucidation by NMR

Heteronuclear single quantum correlation (HSQC) spectra were recorded at a 600 MHz spectrometer (DRX 600, Bruker, Germany) equipped with a single gradient, inverse broadband dual channel probe head. All samples were dissolved in d_8-toluene (Cambridge Isotope Laboratories, Mandover, MA). Spectra were recorded at 325 K. 512 (F1) and 1024 (F2) data points were acquired and 1024 (F1 and 2) processed. The 90 degree pulse length was 8.2 μs. The number of scans was 64 and the acquisition time 85 ms. The total accumulation time was 14 h and 38 min. Xwinnmr 3.1 (Bruker, Germany) was used for evaluation of the obtained spectra.

3.6 Identification and quantification of chloroparaffins

Congener groups were identified by retention time, by signal shape and by correct isotope ratio (Reth and Oehme 2004). The most abundant isotope ion of the $[M\text{-}Cl]^-$ fragment was used for quantification by SIM and the second most intense for abundance confirmation. Response factors of the signal profiles of the $[M\text{-}Cl]^-$ ion clusters were expressed relative to the internal standard $^{13}C_{10}$-*trans*-chlordane or ε-HCH. These data were used uncorrected, since it could be shown that the

correction modes suggested by Tomy *et al.* (1997) had little or no influence on the formula patterns and quantified concentrations (Hüttig and Oehme 2005, Reth *et al.* 2005a). The average molecular mass and average chlorine content were calculated as described by Tomy *et al.* (1997).

The quantification of CPs is more or less strongly dependent on the selected CP standard. This can be explained by different response factors (Zencak 2004). Therefore, different quantification procedures were used for the employed techniques.

ECNI-MS

The quantification of the CPs was performed according to the method described by Reth *et al.* (2004). SCCP (51.5, 55.5 and 63% Cl) and MCCP (42.0, 52.0% and 57.0% Cl) mixtures from Ehrenstorfer (Germany) were used to establish the correlation between the total response factor and the calculated chlorine content. In comparison, sediments were also quantified by technical CP mixtures with similar chlorine content as the samples.

CACI-MS and EI-MS/MS

Quantification of SCCP and MCCP concentrations in sediment samples was carried out using the SCCP (51.5, 55.5 and 63.0% Cl) and MCCP mixtures (47.0, 52.0 and 57.0% Cl) as quantification standards.

3.7 Chemometric methods

The combination of multivariate statistical methods and quantitative trace analysis is still not a common procedure, but provides valuable information especially for monitoring projects. In every monitoring campaign large numbers of samples are analysed in order to assess the composition variability that an environmental system may possess. The large number of samples and the number of constituents to be analysed, results in complex and large data sets being suitable for multivariate statistical processing. Often, important relationships are hidden due to correlations between measured variables thus preventing information from being extracted. Therefore, relationships among such data are sometimes better expressed in terms of similarity or dissimilarity.

3.7.1 Cluster analysis (CA)

The software STATISTICA 5.5 (StatSoft, Inc., Tulsa, USA) was used for multivariate data analysis. Cluster analysis is a popular technique and applied in many fields, such as geochemistry, biology and geology under the name “unsupervised pattern recognition”. The name is given to a set of techniques that seek to determine the structural characteristics of a data set by dividing the data into groups, clusters or hierarchies. Clustering methods are divided again in different categories: hierarchical, object functional and graph theoretical. Hierarchical cluster analysis is the most popular method. Samples within the same cluster are more similar to each other than samples allocated in other/different clusters. Each sample is treated as a point in an *n*-dimensional space. The coordinate axes of this space are defined by the measurements used to characterize the sample. Cluster analysis determines the similarity between the samples by measuring the distances between the data points/samples in the *n*-dimensional space. Similar samples are positioned close to each other and dissimilar samples distant from each other.

There are many possibilities to compute the distances between the samples/data points such as single, complete or average linkage methods. Defining a cluster is the major problem of the hierarchical cluster analysis. Clusters are defined intuitively according to the defined problem and not by a special indicator, which limits the use of this technique. The results of a cluster study are usually displayed as a dendrogram, which is a tree-shaped map of the distances between the data sets. The dendrogram shows the samples (sediments and/or technical CP mixtures) split into clusters at various stages of the analysis.

The data set selected for cluster analysis included different sediment samples and technical CP mixtures characterized by their SCCP and MCCP homologue and congener pattern ($C_{10\text{-}16}Cl_{4\text{-}5\text{-}10}$). The cluster algorithm "complete linkage" was used. The Euclidean distance was calculated to define the distance between clusters.

3.7.2 Principal component analysis (PCA)

The main applications of such factor analysis techniques are: (1) to reduce the number of variables and (2) to detect structures in the relationship between variables. For a principal component analysis of different congener and homologue patterns, the analysed data were organized as a matrix by the software program STATISTICA 5.5 (StatSoft, Inc., Tulsa, USA). Each congener pattern was expressed as an object vector described by N variables. The N variables were the relative abundance of each CP congener ($C_{10\text{-}15/16}$ with 4-10 chlorine atoms). All object vectors (each representing a congener and homologue pattern from different sampled location or a technical CP mixture) were then combined into one matrix. The visualisation of the matrix information becomes difficult, if more than 3 object vectors with more than 3 variables are examined. Then, it is not longer possible to express it in a two- or three-dimensional graphical presentation.

The main use of PCA is to reduce the multidimensionality of a data set, whilst retaining as much information as possible. For this purpose new descriptors are generated called latent variables or principal components (PC). These principal components are linear combinations of the original variable vectors and all are orthogonal (uncorrelated) to each other. The aim of PCA is to present as much as possible of the original data structure/information with a few PC as feasible. The amount of information is quantified by its variance (e.g. how much of the original object vectors can represent or explain). High variance of a principal component suggests high information. The information of two or three PCs can be presented as a two- or three-dimensional plot (score plot). The closer object vectors are to each other in such a score plot, the closer they are correlated.

4 RESULTS AND DISCUSSION

4.1 Method development of chloroparaffins and chlordanes

4.1.1 Linearity, LOD and LOQ

The linearity of a six-point calibration between 2 and 100 ng/µL was good for SCCP ($R^2 > 0.998$) and MCCP (8 points, range 1-100 ng/µL, $R^2 > 0.994$) in the CACI-MS mode. ECNI-MS (Varian 1200L) also showed a sufficient linearity in the range of 1-100 ng/µL for technical SCCP and MCCP mixtures ($R^2 > 0.993$, 7-8 measuring points). Linearity for EI-MS/MS was adequate for a concentration range of 1-100 ng/µL of a technical SCCP mixture with 55.5% Cl and for a technical MCCP mixture with 57% Cl for all CIDs ($R^2 > 0.999$, 7-8 measuring points). In addition, the linearity for ECNI-MS (HP 5989B) was good for eight to ten measuring points for chlordane compounds ($R^2 > 0.99$, 1-6 pg/µL to 5.6 ng/µL depending on the selected compound). Linearity determined by EI-MS/MS and ECNI-MS (Varian 1200L) was comparable for all compounds.

Limits of detection (LOD, S/N 3:1) and quantification (LOQ, S/N 10:1) are given in Table 10 for major congener groups of SCCP and MCCP. The obtained limits were sufficient for the analysis of sediments.

Table 10. Comparison of the calculated limit of detection (LOD, S/N 3:1) and quantification (LOQ, S/N 10:1) for selected SCCP and MCCP compounds (ng/g sediment, dry weight). GC-MS methods using different ionization techniques were applied.

	[ng/g]	$C_{10}H_{16}Cl_6$	$C_{11}H_{18}Cl_6$	$C_{12}H_{20}Cl_6$	$C_{13}H_{22}Cl_6$	$C_{10}H_{15}Cl_7$	$C_{11}H_{17}Cl_7$	$C_{12}H_{19}Cl_7$
ECNI,	LOD	3.1	3.8	3.2	n.a.	n.a.	2.1	3.2
1200L	LOQ	10.3	12.4	10.7			6.8	10.7
ECNI,	LOD	8	3.8	2.8	7.5	9	3.8	3.8
HP 5989B	LOQ	26.5	12.5	9.3	24.8	30	12.5	12.5
CACI	LOD	3.8	1.3	0.8	n.a.	n.a.	1.9	1.3
	LOQ	12.5	4.2	2.5			6.2	4.2
				91→53	102→65	102→67		
EI-MS/MS	LOD			0.6	1.8	0.6		
	LOQ			2.0	5.8	2.0		
		$C_{14}H_{25}Cl_5$	$C_{15}H_{27}Cl_5$	$C_{14}H_{24}Cl_6$	$C_{15}H_{26}Cl_6$	$C_{14}H_{23}Cl_7$	$C_{15}H_{25}Cl_7$	
ECNI,	LOD	10	< 25	1.5	6.1	1.5	2.6	
1200L	LOQ	33.4		4.8	20.5	4.8	8.6	
CACI	LOD	n.a.	n.a.	0.3	1.3	0.4	0.8	
	LOQ	n.a.	n.a.	0.9	4.2	1.3	2.5	
				91→53	102→65	102→67		
EI-	LOD			0.6	2.5	0.6		
MS/MS	LOQ			1.8	8.1	1.8		

n.a. not analysed

Very good results were obtained for the LODs and LOQs of chlordane compounds (see Table 11). Two measuring techniques (ECNI-MS and EI-MS/MS) as well as the results of two mass spectrometers (HP 5989B and Varian 1200L) were compared. The newly developed EI-MS/MS method had comparable detection limits like the ECNI-MS except for *cis*-heptachlorepoxide (*cis*-HEP), where the detectability was higher by one order of magnitude. The use of EI-MS/MS did not lead to an improvement of the limit of detection for the heptachlorepoxides and oxychlordane. For the LODs and LOQs in the technical chlordane mixture one has to consider, that the mixture contains 24% *trans*-chlordane, 19% *cis*-chlordane, 7% heptachlor and *trans*-nonachlor (Dearth and Hites 1991). The LOD and LOQ of *trans*-chlordane in the technical mixture are comparable to the single compound. Both values are three times lower for *cis*-chlordane in technical mixture than for the single compound.

Table 11. Comparison of the limits of detection (LOD) and quantification (LOQ) for chlordane compounds (pg/g sediment). GC-MS methods using different ionization techniques were applied.

	Heptachlor	***trans*-Chlordane**	***cis*-Chlordane**	***trans*-Nonachlor**	***cis*-Nonachlor**	**Oxy-chlordane**	***trans*-HEP**	***cis*-HEP**
				pg/g sediment				
Single compound								
ECNI, HP 5989B								
LOD	8.0	1.0	3.5	1.5	1.0	5.5	14	55
LOQ	26.5	3.5	11.5	4.5	3.5	19.0	47.0	185
ECNI, 1200L								
LOD	6.5	1.8	5.5	1.0	0.5	n.a.	n.a.	n.a.
LOQ	22	6.0	19.0	3.5	2.0	n.a.	n.a.	n.a.
EI-MS/MS								
LOD	2.0	1.0	1.0	1.8	1.8	1.5	12.0	480
LOQ	6.5	3.5	3.5	6.0	6.0	5.5	39.5	1585
Technical mixture								
ECNI, HP 5989B								
LOD	< 8.0	3	4.0	40	60	< 5.5	< 14	< 55
LOQ		12.5	13.5	135	195			
ECNI, 1200L								
LOD	< 6.5	6.5	6.5	70	135	n.a.	n.a.	n.a.
LOQ		21.0	21.0	230	450			

n.a. not analysed

Oxychlordane and *cis*-heptachlorepoxide could not be resolved on DB5-MS (see Figure 3). Elution order of the heptachlorepoxides and oxychlordane as well as co-elution depend on the stationary phase (Karlsson 1998). The mass chromatograms obtained by ECNI-MS are quite similar. The same fragment ions suitable for quantification are present with different abundances in the spectra. Therefore, quantitative analysis of *cis*-heptachlorepoxide is still possible by monitoring the less abundant fragment ion *m/z* 388 for.

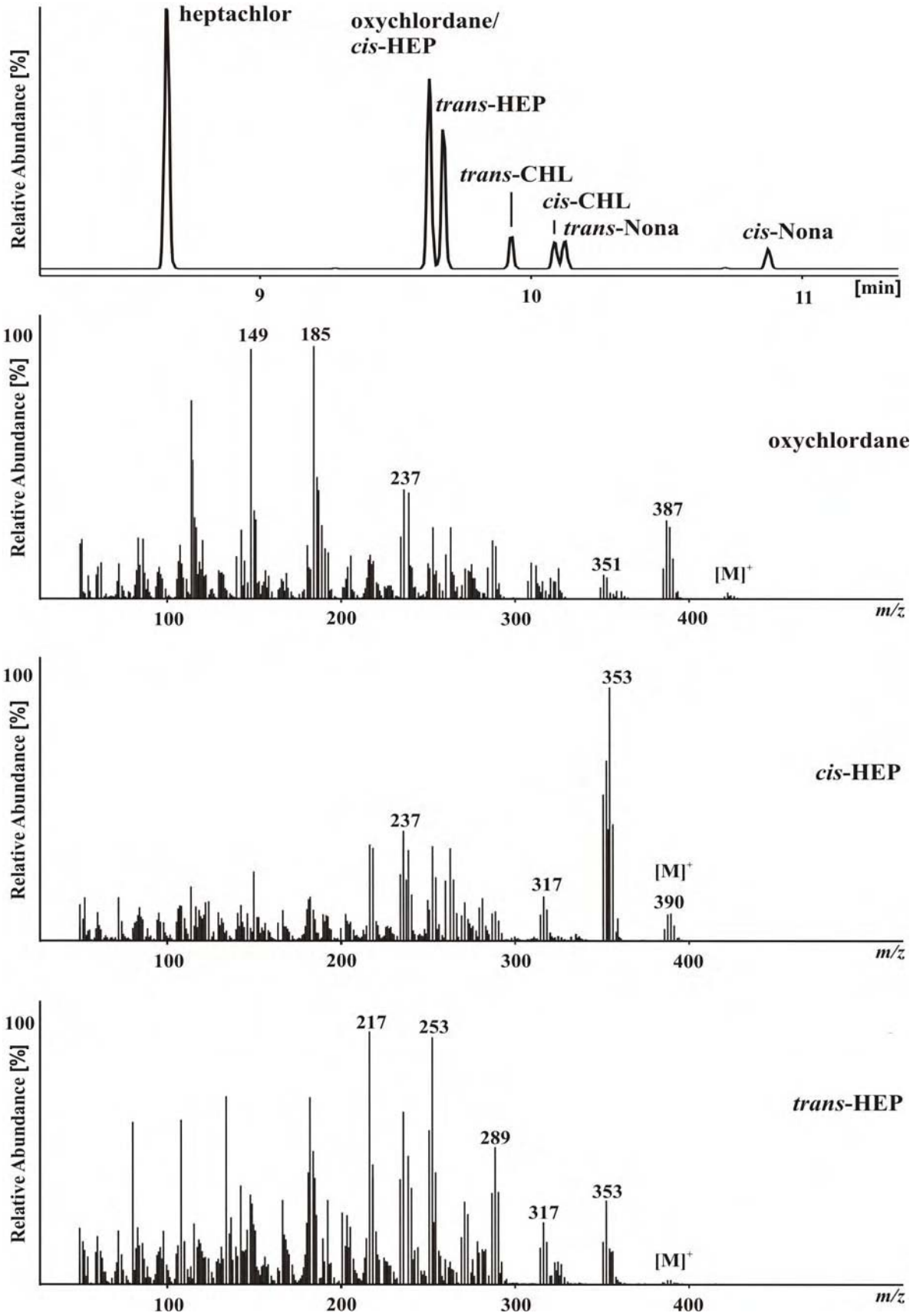

Figure 3. Separation of *cis/trans*-chlordane (CHL), heptachlor, *cis/trans*-heptachlorepoxide (HEP), oxychlordane and *cis/trans*-nonachlor (Nona) by HRGC (DB5-MS). EI-MS full scan spectra of oxychlordane, *cis*- and *trans*-heptachlorepoxide are shown (full scan, *m/z* 50-500).

Chlordane congeners undergo intensive fragmentation under electron impact (EI) conditions (see Figure 3). If present, the molecular peak (*m/z* 390 for *cis/trans*-heptachlorepoxide and *m/z* 424 for oxychlordane) is much less abundant than the fragments. Losses of Cl and HCl from the molecular ion lead to dominant fragments. The EI mass spectra of the two stereoisomers were not identical in this study. The molecular peak of *cis*-heptachlorepoxide is present at low abundance while *trans*-heptachlorepoxide did not generate such a fragment.

The investigated EI-MS/MS fragment of *cis*-heptachlorepoxide (see chapter Experimental) did not lead to an improvement of the quantification limit (see Table 11). ECNI-MS is more sensitive for the detection of this compound although a less abundant mass due to co-elution with oxychlordane can be used for quantitative analysis. EI-MS/MS is more sensitive for the detection of oxychlordane (factor of around 4). No difference was observed for the detection limit of *trans*-heptachlorepoxide.

4.1.2 Method optimization

One aim of this work was to establish a clean-up method as simple as possible and to collect all CPs within one fraction without other interfering contaminants such as toxaphenes, PCBs etc. Soxhlet extraction in combination with a further fractionation step on alumina, silica or Florisil® led to sufficient CP recoveries (Parera *et al.* 2002, Zitko 1973). A further clean-up step was necessary for sediments with higher total organic carbon content (TOC). Sample matrix, not persistent to sulphuric acid, was removed prior to the Florisil® clean-up. Recoveries of selected SCCP and MCCP compounds as well as internal standard (ISTD) after different steps of the clean-up procedure are given in Table 12 and Figure 4.

Table 12. Recovery [%] of SCCP compounds and ^{13}C-*trans*-chlordane (ISTD) after different steps of the sample clean-up (total 1500 ng technical SCCP mixture with 55.5% chlorine content).

	Recovery [%]						
	^{13}C-*trans*-Chlordane	**$C_{10}H_{16}Cl_6$**	**$C_{11}H_{18}Cl_6$**	**$C_{11}H_{17}Cl_7$**	**$C_{12}H_{20}Cl_6$**	**$C_{12}H_{19}Cl_7$**	**$C_{13}H_{22}Cl_6$**
Extraction (Sand)							
1 [a]	84	101	105	n.a.	91	n.a.	116
2 [a]	78	96	97	n.a.	90	n.a.	98
	81±3	99±3	101±4	n.a.	91±1	n.a.	107±9
Extraction (Sodium sulphate)							
1	69	n.a.	97	78	82	78	n.a.
2	64	n.a.	100	81	101	85	n.a.
3	74	93	88	84	93	96	97
	69±4		95±5	81±2	92±8	86±7	n.a.
Adsorption chromatography with Florisil®							
1 [b]	88	n.a.	101±9 [c]	109±11 [c]	109±12 [c]	109±12 [c]	n.a.
2	75	n.a.	82	82	81	86	n.a.
3	88	n.a.	90	87	83	96	n.a.
	82±7	n.a.	86±4	85±3	81±2	91±5	n.a.
Clean-up (Sodium sulphate)							
1 [b]	75	n.a.	95	96	100	102	n.a.
Clean-up (Sand)							
1	75	73	81	n.a.	75	101	n.a.
2	69	54	63	n.a.	60	71	n.a.
3	73	79	78	n.a.	86	94	n.a.
4	76	97	89	n.a.	101	115	n.a.
	73±3	76±15	78±9	n.a.	81±15	95±16	n.a.

[a] with addition of copper, [b] total 5000 ng SCCP with 55.5% Cl, [c] five parallel measurements; n.a. not analyzed

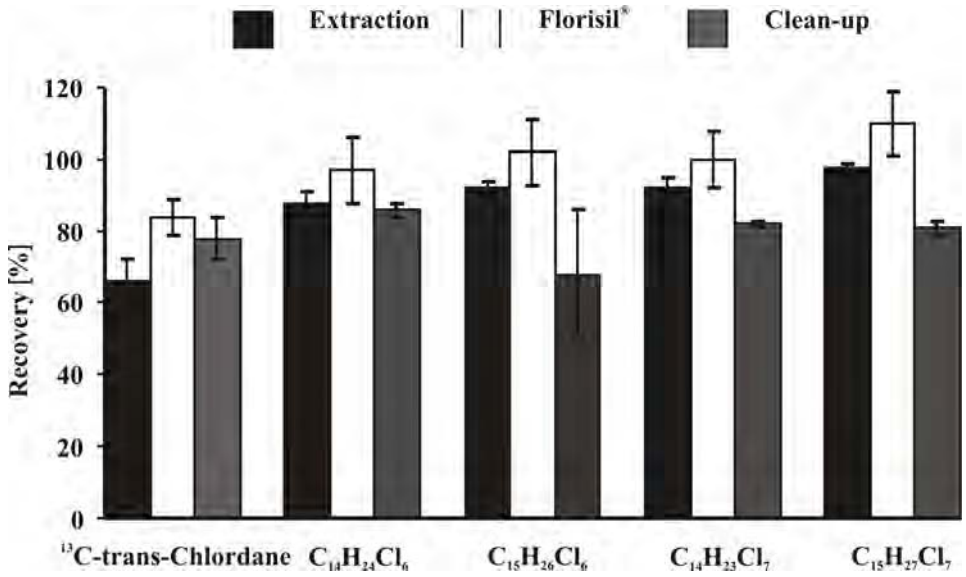

Figure 4. Recovery [%] of selected MCCP compounds and ^{13}C-*trans*-chlordane after different clean-up steps (matrix: 20 g of calcined sand; total amount of 1500 ng MCCP with 52% Cl). Clean-up included extraction, column chromatography with Florisil® and silica gel.

Several aliquots of North Sea sediment were spiked different times with variable amounts of SCCPs and MCCPs to determine the recovery of the target compounds. All samples were Soxhlet extracted, the extracts were cleaned with a silica gel column and fractionated on a Florisil® column. The recoveries are shown in Table 13. They were sufficient for the determination of CPs in sediment samples and comparable to those of the different internal standards. It was necessary to reduce the extract volume to 50 µl (normally 150-200 µl) in order to detect low amounts of SCCP and MCCPs (100 ng each) by ECNI-MS. The suitability of ^{13}C-*trans*-chlordane, octachloronaphthaline (OCN) as well as MC8 (chlordane compound) as ISTD was shown. In theory, the recovery of ISTD should be comparable with the CP recoveries (± 10%). ^{13}C-*trans*-Chlordane was chosen as ISTD for the CP quantification (Table 13). However, the recoveries of OCN and MC 8 were checked additionally for sediments.

Table 13. Clean-up recoveries [%] of ISTDs and selected SCCP and MCCP congeners in spiked North Sea sediments (10-20 g).

	Recovery [%]						
	$^{13}C_{10}$-*trans*-Chlordane	OCN	MC8	$C_{10}H_{16}Cl_6$	$C_{11}H_{17}Cl_7$	$C_{14}H_{24}Cl_6$	$C_{15}H_{26}Cl_6$
Clean-up (Matrix: North Sea sediment I)							
1	72	85	*	< LOD	< LOD	< LOD	< LOD
2 [a]	77	87	82	120	95	57	71
3 [b]	72	88	73	84	81	117	126
4 [c]	67	82	79	120	112	90	114
Clean-up (Matrix: North Sea sediment II)							
1	80	74	74	< LOD	< LOD	< LOD	< LOD
2 [c]	77	93	74	105	102	n.a.	n.a
				$C_{11}H_{17}Cl_7$	$C_{12}H_{19}Cl_7$	$C_{14}H_{23}Cl_7$	
1 [d]	78±8	*	*	96±7	88±8	74±13	

[a] with 500 ng of SCCP with 63% Cl and of MCCP with 52% Cl each; [b] with 1000 ng of SCCP with 63% Cl and of MCCP with 52% Cl each ; [c] with 1500 ng of SCCP with 63% Cl and of MCCP with 52% Cl each; [d] with 100 ng of SCCP 63% Cl and 100 ng of MCCP 57% Cl each, four clean-ups in parallel; * not added; LOD: limit of detection (see table 10)

High resolution MS (HRMS, resolution of 12'000) is often used for CP analysis to avoid interferences from other chlorinated compounds with the same mass-to-charge ratio and retention time range (Tomy *et al.* 1997). However, recent publications showed that LRMS can be used instead (Castells *et al.* 2004, Zencak *et al.* 2005). This requires an efficient sample clean-up (Parera *et al.* 2004, Reth *et al.* 2005a). Stejnarova *et al.* (2005) also emphasised the need of a complete elimination of interfering substances, especially toxaphene and PCBs.

The applied Florisil® column enabled the removal of toxaphenes, DDT-compounds, PCB and heptachlor as tests with model compounds demonstrated (Table 14). These substances eluted completely in the first fraction. α-HCH, *cis/trans*-chlordane and *cis*-nonachlor as well as CPs were part of the second fraction of the Florisil® column. *trans*-Nonachlor was found in both.

Table 14. Distribution of model compounds, chlordanes and ISTDs [%] between the two fractions of the Florisil® column chromatography.

	Distribution [%]	
	Fraction 1 (60 ml *n*-hexane and 5 ml DCM)	**Fraction 2 (55 ml DCM)**
α-HCH [a]	6±9	94±9
^{13}C-*trans*-Chlordane (ISTD) [a]	23±11	77±11
PCB 153 [a]	100±1	< LOD
p,p`-DDT [a]	103±4	< LOD
Toxaphen #44 [a]	95±2	5±1
^{13}C-*trans*-Chlordane (ISTD) [b]	< LOD	89±5
OCN (ISTD) [b]	< LOD	105±2
MC8 (ISTD) [b]	2±2	93±11
4,5-DCCD (ISTD) [b]	85±9	7±5
trans-Chlordane [b]	2±2	90±7
cis-Chlordane [b]	< LOD	84±7
Heptachlor [b]	81±20	3±2
cis-Nonachlor [b]	1±1	89±6
trans-Nonachlor [b]	49±8	37±8

[a] mean± standard deviation of 4 measurements; [b] mean ± standard deviation of 3 measurements; ISTD internal standard; LOD limit of detection

Most of the interesting chlordanes eluted in the same fraction as CPs as can be seen from Table 14. It was impossible to elute *trans*-nonachlor within one fraction, therefore *trans*-nonachlor concentrations were quantified in both. Recovery rates of oxychlordane and *cis/trans*-HEP were in the range 70-80% after Florisil® column. However, the three substances were not stable to acid treatment during sample clean-up as reported by Karlsson (1998). The epoxide bridge over C2 and C3 is not stable in the presence of acid. 4,5-Dichlorochlordene was selected as ISTD for fraction I and ^{13}C-*trans*-chlordane for fraction II. The recoveries after the complete clean-up procedure (soxhlet extraction, silica gel column and adsorption chromatography on Florisil®) were lower than CP recoveries (see Table 15). Recoveries of chlordane compounds in fish samples were in the same range (Karlsson 1998). The recovery rate of internal standards added before sample extraction/clean-up should be within the range 50-100% (Oehme 1998). It was found that the

recoveries of both internal standards were sufficient. Furthermore, ^{13}C-*trans*-chlordane and 4,5-dichlorochlordene belong to chlordane and should behave nearly identically during sample clean-up as the chlordane compounds analyzed.

Table 15. Recoveries [%] of chlordane compounds and internal standards after complete sample clean-up.

	Recoveries [%]				
	Sand	**Sand**	**North Sea sediment spiked with chlordanes and ISTD**		
ISTD					
$^{13}C_{10}$-*trans*-Chlordane	68	77	72	75	86
OCN	94	92	93	100	88
MC8	81	85	79	75	89
4,5-DCCD	49	68	68	92	85
Chlordane					
trans-Chlordane	70	77	67	75	86
cis-Chlordane	74	82	59	75	85
Heptachlor	63	60	60	92	73
trans-Nonachlor	75	74	66	78	86
cis-Nonachlor	78	84	54	74	81

4.2 Quantification

4.2.1 Comparison of applied CP methods

Eleven sediment samples collected in 2003 and 2004 were analyzed by CACI-MS, ECNI-MS and EI-MS/MS. ECNI-MS quantifications were carried out by both the conventional procedure (comparison with a standard of similar chlorine content) and the quantification approach according to Reth *et al.* (2005) for ECNI-MS. Quantification by EI-MS/MS was performed with a MCCP standard containing 57% Cl. Three SCCP (51.5, 55.5 and 63% Cl) as well as with three MCCP (47, 52 and 57% Cl) standards were applied for CACI-MS. The results are compared in Table 16.

The total CP concentrations (SCCP+MCCP) obtained by the different ionization techniques (EI-MS/MS, CACI-MS and ECNI-MS) and two applied quantification procedures showed a relative standard deviation of ≤ 34% for sediments. All concentrations obtained by CACI-MS were higher than those determined by ECNI-MS. CACI-MS allows the determination of lower chlorinated compounds not detectable by ECNI-MS (see chapter Introduction). However, less chlorinated SCCPs and MCCPs were the main components in sediments (see next chapter). Moreover, EI-MS/MS quantification was not disturbed by any interfering substances. The obtained concentrations were in the same range as for CACI-MS. Results obtained by both quantification procedures applied for ECNI were in very good agreement (relative standard deviation < 12%).

Variance analysis of the obtained mean concentrations showed no significant difference for the three different ionization techniques and two quantification procedures (Danzer *et al.* 2001). This is caused by the high standard deviations of each method. Table 16 shows also two samples (KS 8 (2004) and ODER), where EI-MS/MS and CACI-MS results were twice as high for ECNI-MS.

Table 16. Comparison of CP quantification (ng/g dry weight, sum of S+MCCP) of sediments by three mass spectrometric methods.

Sample	EI-MS/MS [a]	CACI-MS [b]	ECNI-MS [c]		
			Comparison with standard	According to Reth *et al.* (2004)	Mean±Standard deviation
	S+MCCP [ng/g dry weight]				
KS 8 (2003)	125	106	90	114	109±15
KS 8 (2004)	211	211	102	91	154±66
KS 11 (2003)	77	76	52	47	63±16
KS 11 (2004)	290	324	224	212	263±53
710 (2004)	37	50	30	38	39±8
715 (2004)	68	89	63	65	71±12
718 (2004)	176	231	125	138	168±48
721 (2004)	105	125	86	99	104±16
ODER	59	61	29	30	45±18
RUDEN	107	86	76	59	82±20
ECKFBU	124	106	86	70	97±24
Mean±Standard deviation	125±75	133±86	88±54	88±53	

[a] quantification with MCCP standard of 57% Cl; [b] average ; [c] $C_{10\text{-}15}Cl_{5\text{-}10}$ determined

Especially, the detection of lower chlorinated CP (Cl_5 and Cl_6) compounds by ECNI-MS was disturbed by interfering compounds not removed by sample clean-up (see Chapter 4.4.4). Therefore, interpretation of the obtained chromatograms was not possible. However, as later shown, these CPs compounds with 5 and 6 chlorine atoms were the main components in sediments. Since these compounds were not included into quantification due to interferences analysis by ECNI-MS results in lower concentrations as CACI-MS and EI-MS/MS.

Higher deviations were also reported for spiked fish samples (Zencak, 2005). Relative standard deviations of less than 30% were considered to be acceptable taking the interday reproducibility (< 28% for SCCPs and < 18% MCCPs, depending on the applied MS technique) into account.

Additionally, eighteen sediment and suspended particular matter samples were analyzed by HRGC-ECNI-MS, and their chlorine content was determined according to Tomy *et al.* (1997). It varied between 58-64% Cl for SCCPs and between 53-58% for MCCPs. SCCP standards with 55.5 and 63% Cl as well as MCCP standards with 52 and 57% Cl were selected for quantification. The commercially available SCCP and MCCP standards from Ehrenstorfer (Germany) were used to establish the linear correlation. The correlation coefficient was always > 0.9. Results of both methods are shown in Table 17.

Both quantification procedures led to comparable results. Deviations of the S+MCCP results were mainly < 30%. Table 17 also shows two samples (Hamburg 1, Hamburg 2 and Elbe), where the S+MCCP results obtained by both quantification procedures differed < 58%, respectively. MCCP concentrations obtained by the conventional quantification procedure were around 75% higher than those obtained by the new quantification approach. The calculated chlorine content of these samples (55%) was not comparable to the applied MCCP standard (47% Cl). However, the commercial available MCCP standard solution with 52% Cl could not be used for quantification of the samples 1-9 in table 17 (method II) due to differences in the CP pattern and response factor (see Figure 7). Therefore, results were slightly overestimated for the nine samples.

Table 17. Comparison of SCCP, MCCP and S+MCCP concentrations [ng/g dry weight] for river sediments and suspended particular matter obtained by ECNI-MS and quantified by two methods.

Sample	SCCP [ng/g d.w.]		MCCP [ng/g d.w.]		S+MCCP [ng/g d.w.]	
	Method I [a]	Method II [b]	Method I [a]	Method II [b]	Method I [a]	Method II [b]
Seine estuary 1	51	35	85	130	136	165
Seine estuary 2	41	24	24	29	65	121
Seine estuary 3	28	21	58	79	86	100
Hamburg 1	75	90	153	271	228	361
Hamburg 2	67	69	98	143	165	212
Hamburg 3	47	50	75	129	122	179
Tromsø 1	66	60	137	178	203	238
Tromsø 2	21	17	63	45	84	62
Elbe	46	46	116	167	162	213
Neckar 1						
August	81	77	124	110	205	187
September	53	51	85	70	138	121
November	78	83	112	103	190	186
December	79	81	407	416	486	497
Neckar 2						
August	366	329	1081	848	1447	1177
September	144	170	215	170	359	340
Rhine						
August	47	43	124	95	171	138
September	22	17	54	44	76	61
December	43	41	124	92	167	133

[a] Quantification according to Reth *et al.* (2004); [b] Quantification with SCCP and MCCP standards of similar chlorine content, according Tomy *et al.* (1997)

No correlation between the chlorine content of technical SCCP and MCCP mixtures and the response factor was observed when methane/dichloromethane as reagent gas mixture was applied (see Figure 5). Cereclor^{TM} 70L with the highest chlorine content had the lowest response of technical SCCP mixtures. A factor of at maximum 1.5 was found for technical MCCP mixtures. Therefore, the quantification procedure according to Tomy *et al.* (1997) was always applied for CACI-MS. Results of this procedure obtained with different SCCP and MCCP mixtures as quantification standards are shown in Table 18. Differences of < 25% were observed.

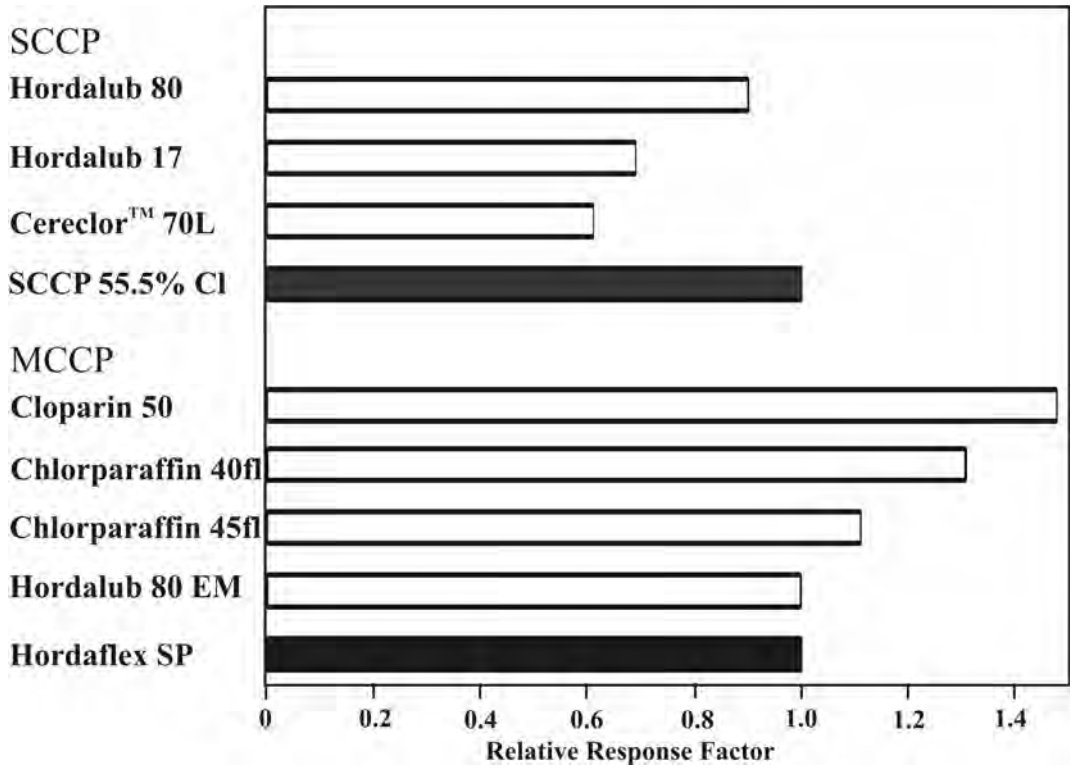

Figure 5. Relative response factors of technical SCCP and MCCP mixtures (normalized to SCCP with 55.5 % Cl and for MCCPs to Hordaflex SP as references) obtained by CACI-MS. Response factors were calculated on mass basis using the sum of the signals of all congeners.

Table 18. Determination of CP concentrations [ng/g dry weight] in sediments based on three different SCCP and MCCP (C_{14-16}) mixtures as reference standard. Mean and standard deviation are given. HRGC-CACI-LRMS was employed and quantification was carried out according to Tomy *et al.* (1997).

Standard	**SCCP 51.5% Cl**	**SCCP 55.5% Cl**	**SCCP 63% Cl**	**Mean±Standard deviation**
Sample		**[ng/g dry weight]**		
KS 8 (2003)	33	31	27	30±2
KS 8 (2004)	63	75	46	62±12
KS 11 (2003)	19	22	14	18±3
KS 11 (2004)	86	79	70	79±6
710 (2004)	14	16	10	13±3
715 (2004)	38	35	31	35±3
718 (2004)	89	82	73	82±7
721 (2004)	48	44	39	44±4
ECKFBU (2004)	32	29	26	29±2
ODER (2004)	18	22	13	18±3
RUDEN (2004)	26	31	19	25±5
Standard	**MCCP 47% Cl**	**MCCP 52% Cl**	**MCCP 57% Cl**	
KS 8 (2003)	80	81	66	76±7
KS 8 (2004)	151	148	149	149±1
KS 11 (2003)	58	57	57	58±1
KS 11 (2004)	291	295	239	275±25
710 (2004)	45	38	30	37±6
715 (2004)	57	59	45	54±6
718 (2004)	158	164	125	149±17
721 (2004)	86	89	68	81±9
ECKFBU (2004)	81	87	67	77±7
ODER (2004)	43	42	43	43±1
RUDEN (2004)	62	61	61	61±1

Similar to CACI-MS, the use of EI-MS/MS showed low variation of the response factors (at maximum factor 3) for technical SCCP, MCCP, mixtures of both as well as LCCP mixtures (see Figure 6). Very low reponse factors compared to SCCP with 55.5% Cl were found for LCCP with 36% Cl, Hordalub 500, Cereclor 70L and Cloparin 60. Replicate analyses (deviations < 8% depending on the selected CID) showed no changes. No correlation between the chlorine content and the response factor was observed.

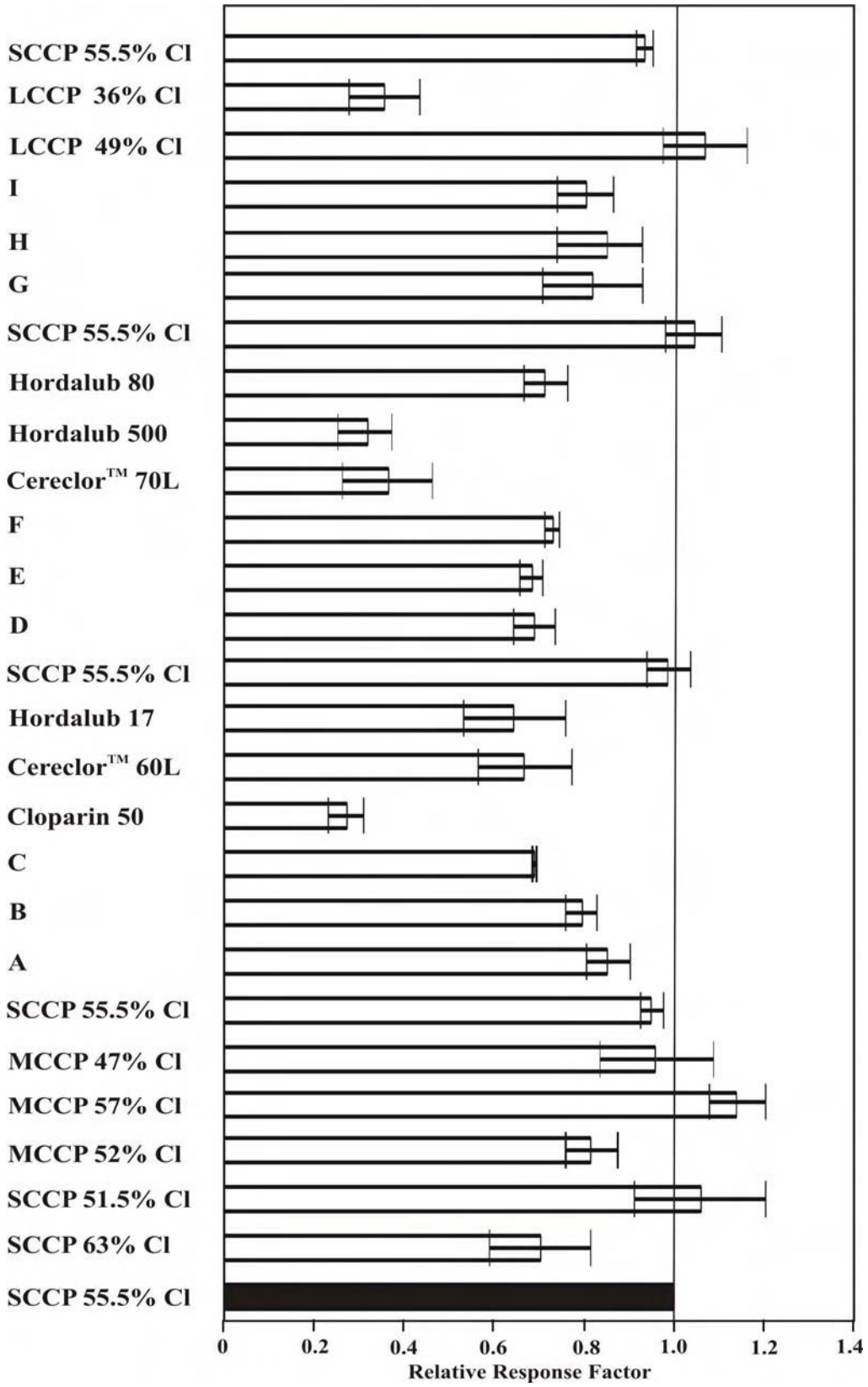

Figure 6. Relative response factors of technical SCCP, MCCP and LCCP mixtures (normalized to SCCP with 55.5 % Cl) obtained by EI-MS/MS. The mean and standard deviation of the response factors of the three fragmentations m/z 102 to 67, 102 to 65 and 91 to 53 are shown. A total CP amount of 1500 ng was obtained by mixtures of Hordalub 80 and MCCP with 52% Cl 1:2 (A), 1:1 (B), 2:1 (C), by a mixture of Hordalub 80 and Hordalub 80 EM 1:2 (D), 1:1 (E), 2:1 (F) as well as by a mixture of Hordalub 80 and MCCP with 47% Cl 1:2 (G), 1:1 (H) and 2:1 (I).

The results of this chapter can be summarized as follow:

- S+MCCP concentrations obtained by three different ionization techniques (EI-MS/MS, CACI-MS and ECNI-MS) were comparable for the analysis of sediments with satisfying accuracy.
- SCCP and MCCP concentrations obtained by the usual quantification procedure (comparison with a standard of similar chlorine content, according to Tomy *et al.* 1997) and the quantification approach according to Reth *et al.* (2004) were in very good agreement for sediments (ECNI-MS).
- The influence of the chlorine content on the response factor of SCCP and MCCP mixtures with varying chlorine content was small when CACI-MS was applied. The selected quantification standard had therefore little influence on the CP concentrations in sediments. Quantification was always carried out using the procedure according to Tomy *et al.* (1997).
- EI-MS/MS showed higher variations of the response factors than CACI-MS. However, these differences are acceptable for a screening method. The application of the new quantification approach according to Reth *et al*. (2004) was not necessary.

4.2.2 Comparison of chlordane concentrations obtained by different methods

Results obtained by the newly developed EI-MS/MS method and by ECNI-MS on two different instruments were compared (see Tables 19 and 20). Relative standard deviations varied between 7-9% for heptachlor, 5-39% for *trans*-chlordane, 8-36% for *cis*-chlordane, 8-13% for *trans*-nonachlor and 6-29% for *cis*-nonachlor. Deviations between 7-88% were observed for samples KS 11 (2003) and 710 (2004) due to concentrations close to the limit of quantification and were therefore considered as acceptable (see Table 11).

Table 19. Comparison of chlordane concentrations [pg/g dry weight] of selected sediments obtained by different HRGC-LRMS methods.

Sample	Method	Heptachlor	*trans*-Chlordane	*cis*-Chlordane	*trans*-Nonachlor	*cis*-Nonachlor
Florisil® fraction		**F1**	**F2**	**F2**	**F2**	**F2**
				[pg/g dry weight]		
710 (2004)	EI-MS/MS	< 2	5	3	139	< 1.8
	ECNI, 1200L	< 6.5	< 1	< 6	127	< 0.5
	ECNI, HP 5989B	< 8	6	8	118	2
	Mean ± standard deviation		5±1	8±4	128±9	4±3
715 (2004)	EI-MS/MS	< 2	47	27	58	23
	ECNI, 1200L	< 6.5	49	38	54	24
	ECNI, HP 5989B	< 8	42	31	52	21
	Mean ± standard deviation		46±3	32±5	53±5	23±1
718 (2004)	EI-MS/MS	< 2	72	49	114	49
	ECNI, 1200L	< 6.5	54	51	123	26
	ECNI, HP 5989B	< 8	47	41	110	19
	Mean ± standard deviation		58±11	47±4	116±5	31±13
721 (2004)	EI-MS/MS	54	153	116	131	39
	ECNI, 1200L	61	142	141	104	34
	ECNI, HP 5989B	64	135	126	97	29
	Mean ± standard deviation	56±5	143±7	128±10	110±14	34±4
ECKFB U (2004)	EI-MS/MS	< 2	47	33	167	32
	ECNI, 1200L	< 6.5	44	54	149	27
	ECNI, HP 5989B	< 8	36	35	136	19
	Mean ± standard deviation		42±5	41±9	150±10	26±5
ODER (2004)	EI-MS/MS	56	66	83	115	21
	ECNI, 1200L	36	78	44	104	26
	ECNI, HP 5989B	42	59	60	93	17
	Mean ± standard deviation	45±8	68±8	62±16	103±12	21±4

Table 20. Comparison of chlordane concentrations [pg/g dry weight] of selected sediments obtained by different HRGC-LRMS methods.

Sample	Method	Heptachlor	*trans*-Chlordane	*cis*-Chlordane	*trans*-Nonachlor	*cis*-Nonachlor
Florisil fraction		**F1**	**F2**	**F2**	**F2**	**F2**
				[ng/g dry weight]		
RUDEN (2004)	EI-MS/MS	< 2	18	23	196	11
	ECNI, 1200L	< 6.5	14	25	161	13
	ECNI, HP 5989B	< 8	6	16	150	6
	Mean ± standard deviation		13±5	21±4	170±20	10±3
KS 8 (2003)	EI-MS/MS	< 2	20	11	86	< 1.8
	ECNI, 1200L	< 6.5	18	28	71	12
	ECNI, HP 5989B	< 8	16	19	64	8
	Mean ± standard deviation		18±2	19±7	74±2	9±2
KS 8 (2004)	EI-MS/MS	< 2	27	32	188	6
	ECNI, 1200L	< 6.5	24	18	168	< 0.5
	ECNI, HP 5989B	< 8	21	18	155	6
	Mean ± standard deviation		24±2	23±7	170±14	5±1
KS 11 (2003)	EI-MS/MS	[a]	17	7	212	< 1.8
	ECNI, 1200L	[a]	34	35	228	38
	ECNI, HP 5989B	[a]	13	10	193	5
	Mean ± standard deviation		21±9	17±13	211±14	17±15
KS 11 (2004)	EI-MS/MS	[a]	31	23	[a]	19
	ECNI, 1200L	[a]	28	[a]	[a]	[a]
	ECNI, HP 5989B	[a]	27	35	[a]	12
	Mean ± standard deviation		29±2	29±6		16±4

[a] integration partly not possible due to interferences

4.3 Characterization of technical chloroparaffin mixtures

Commercial chlorinated paraffins are very complex mixtures with the general formular $C_nH_{2n+2-x}Cl_x$. They are usually characterized by the length of the carbon chain (e.g. C_{10-13} for SCCPs) and the average chlorine content. The amount of chlorine present is usually expressed as weight percentage (% Cl). The CP composition can vary for a given chlorine content depending on chain length range, producer, batch etc. (see Figure 7).

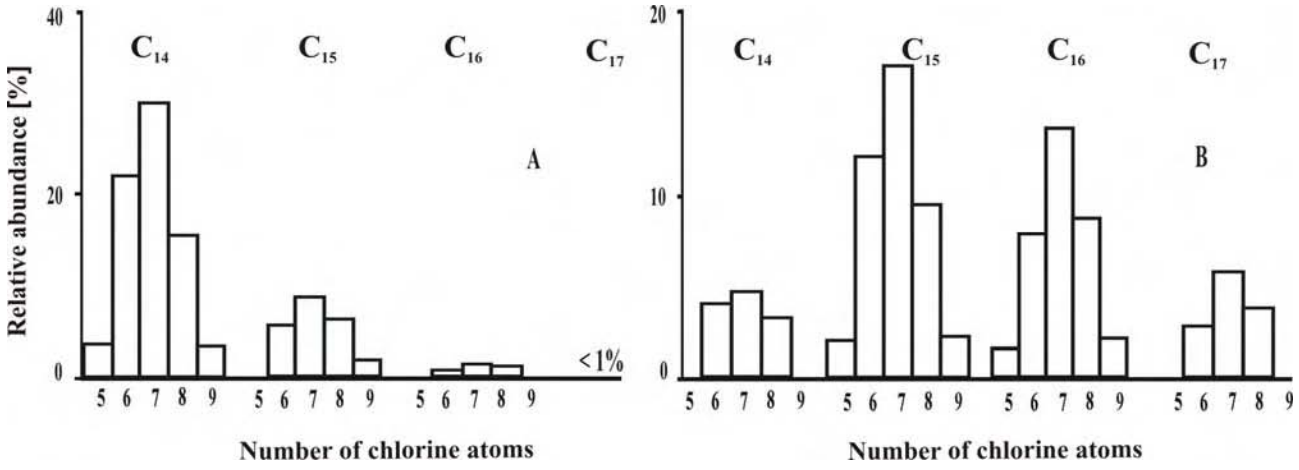

Figure 7. Two MCCP mixtures (Ehrenstorfer, Germany) with a chlorine content of 52% Cl (A: calculated molecular mass of 439 g/mol and chlorine content of 55% and B: 456 g/mol and 54%). Data were obtained by ECNI-MS.

GC-MS analysis of commercial SCCP mixtures showed that decanes, undecanes and dodecanes with six and seven chlorine atoms are predominant (Tomy *et al.* 1997). Unfortunately, standard analytical methods do not permit the separation of the thousands of different CP congeners in a technical mixture and, therefore, the actual substitution pattern on the carbon chain is unknown (Tomy *et al.* 1998a).

Since a precise determination of the composition of a CP mixture is impossible with the currently available techniques, the work in the following two chapters discusses principal differences and similarities in the relative distribution of congeners and homologues evaluated by cluster analysis. Homologue and congener group composition of technical mixtures and commercially available SCCP and MCCP solutions were determined by HRGC-ECNI-LRMS and HRGC-CACI-LRMS for this purpose.

4.3.1 ECNI-LRMS

Figure 8 shows the dendrogramms of the cluster analysis of technical SCCP mixtures and the commercially available SCCP and MCCP standards from Ehrenstorfer. The SCCP mixtures were separated into two main clusters (cluster I: Cereclor^{TM} 70L, Hordalub 500 and SCCP 63% Cl; cluster II: SCCP 51.5% Cl, Hordalub 17, SCCP 55.5%, Hordalub 80 and Cereclor^{TM} 60L. Also the dendrogramm of the MCCP mixtures shows two main clusters (cluster I: MCCP 47% Cl, Chlorparaffin 40fl, Cereclor S52, MCCP 52% Cl, Cloparin 50 and Hordalub 80 EM; cluster III: MCCP 57% Cl and Hordalflex SP). Chlorparaffin 45fl was separated from both clusters. The main criterion of differentiation was the degree of chlorination (see Table 21). The SCCP mixtures were separated into two groups having a chlorine content ≤ 60% and > 60% and the MCCPs into ≤ 50% Cl and > 50% Cl.

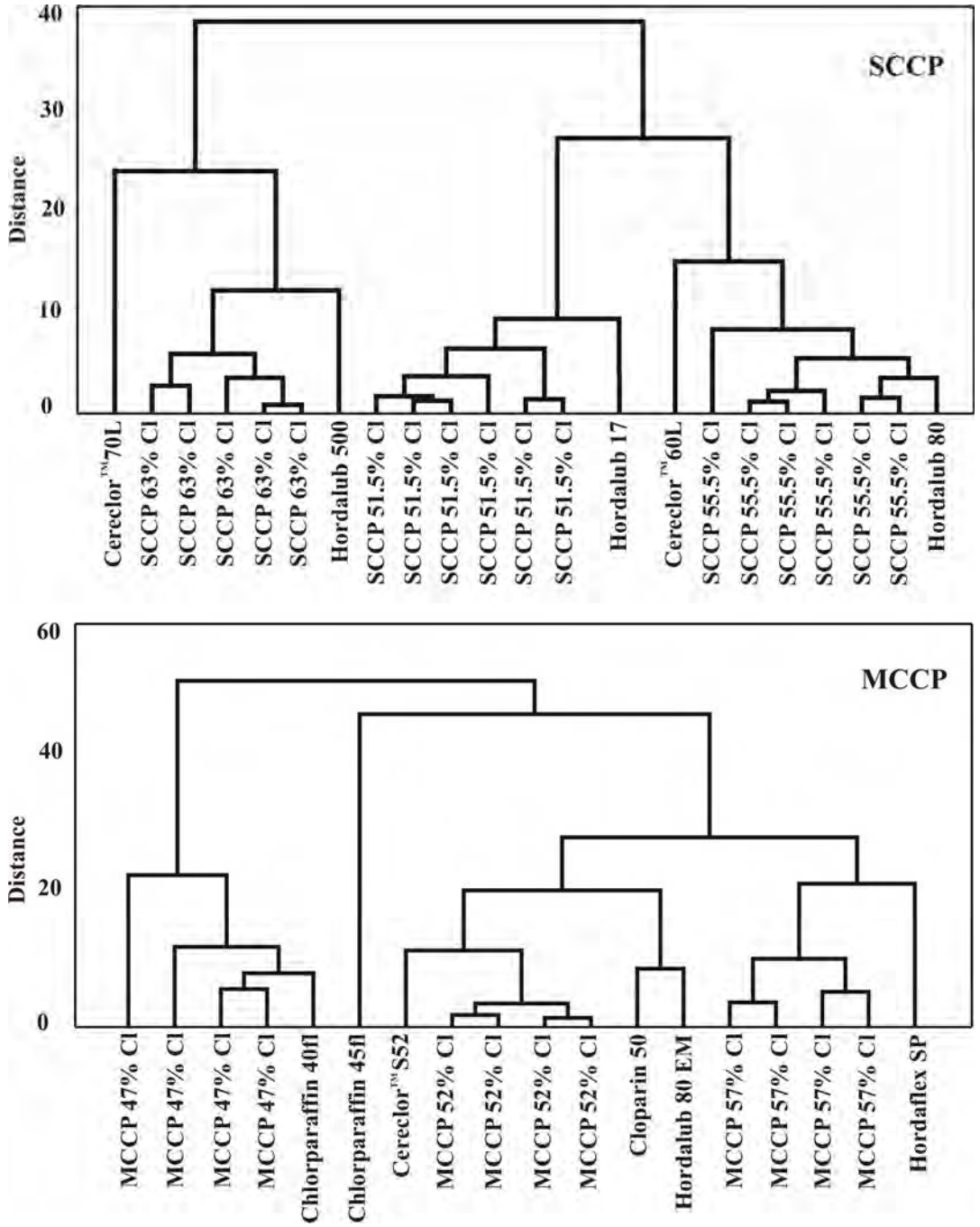

Figure 8. Complete linkage dendrogramm (Euclidian distance) of technical SCCP and MCCP mixtures (for data see Table 24). Homologue and congener group composition was obtained by HRGC-ECNI-LRMS.

Table 21. Composition of technical SCCP and MCCP mixtures (concentration of 7.5 ng/µL) determined by HRGC-ECNI-LRMS. Information is given about the specified and calculated average chlorine content [% Cl], the calculated average molecular mass [g/mol], distribution of C_{10-13} and C_{14-16} congeners with 5-10 chlorine atoms [%].

Mixture	Chlorine content [% Cl]		Molecular mass [g/mol]	Distribution [%]				Main components	
	specified	calculated	calculated	C_{10}	C_{11}	C_{12}	C_{13}	$C_{11}Cl_x$	$C_{12}Cl_x$
SCCP 51.5% Cl [a]	51.5	57.5±0.2	384±4	5±1	28±2	38±1	30±2	5/6	6/7
SCCP 55.5% Cl [a]	55.5	59.2±0.1	396±2	6±1	32±3	38±2	24±3	6/7	7/8
SCCP 63.0% Cl [a]	63.0	62.9±0.1	432±12	7±1	35±2	34±2	24±1	7/8	7/8
Hordalub 17	49.0	56.7	375	6	32	34	28	5/6	5/6
Hordalub 80	56.0	59.6	397	7	35	35	22	6/7	6/7
Cereclor™ 60L	59.0	61.1	414	11	26	37	26	7/8	7/8
Hordalub 500	62.0	63.2	425	9	48	32	11	7/8	7/8
Cereclor™ 70L	69.0	65.2	460	13	27	35	26	[b]	9/10
				C_{14}	C_{15}	C_{16}	C_{17}	$C_{14}Cl_x$	$C_{15}Cl_x$
MCCP 47% Cl [a]	47.0	52.2±0.3	413±4	68±6	30±5	2±2	n.a.	5/6	6/7
MCCP 52% Cl [a]	52.0	55.7±0.1	443±1	71±1	25±1	4±1	n.a.	6/7	7/8
MCCP 57% Cl [a]	57.0	57.5±0.2	466±4	65±6	24±2	11±6	n.a.	7/8	7/8
Chlorparaffin 40fl	41.0	51.6	412	62	29	10	n.a.	5/6	5/6
Chlorparaffin 45fl	46.0	51.1	430	13	46	39	n.a.	[c]	6/7
Hordalub 80 EM	49.0	53.7	438	46	33	20	n.a.	6/7	6/7
Cloparin 50	51.0	54.4	439	57	28	15	n.a.	6/7	6/7
Cereclor™ S52	52.0	56.0	450	66	27	7	n.a.	6/7	7/9
Hordaflex SP	56.0	56.7	469	39	39	23	n.a.	7/8	7/8

[a] mean of 4-5 measurements at different days; n.a. not analysed; [c] $C_{13}Cl_{9/10}$ are main components, [b] $C_{16}Cl_{6/7}$ are main components

At a first glance, it is not clear why the MCCP mixture Chlorparaffin 45fl with a specified chlorine content of 46% was also part of cluster II, which should contain compositions having a chlorine content > 50%. As can be seen from Table 21, CH_4-ECNI overestimated the chlorine content for the mixtures except Cereclor™ 70L. The deviations varied between 0-16% for SCCPs and between 1-26% for MCCPs. They were higher for SCCP (4-16%) and MCCP (11-26%) mixtures being part of

cluster I. This difference could be due to the content of tri- and tetrachlorinated congeners, which are not detectable by CH_4-ECNI.

Members of the same cluster also had similar molecular mass, main formula/congener components as well as similar CP patterns (see Table 21). However, Cereclor^{TM} 60L showed a more similar CP pattern and chlorine content than Hordalub 80 and SCCP 55.5%. The main components, the calculated chlorine content and molecular mass were similar to mixtures with a higher chlorine content. This observation is in contrast to earlier published results, where Cereclor^{TM} 60L was classified in the group with a calculated chlorine content > 61 % (Hüttig and Oehme 2005). One explanation might be the use of a different MS system for these data. Only the MCCP mixture Chlorparaffin 45fl showed higher relative abundances of C_{15} and C_{16} than C_{14} components (see Table 21). Main components, the calculated chlorine content as well as the molecular mass were similar to MCCP 47% Cl and Chlorparaffin 40fl.

Data from suppliers were hardly available. The molecular weight of Cereclor^{TM} 60L, 70L and S52 were specified as 398, 503 and 422 g mol^{-1} for production years 1999/2000 (Ineos Chlor Limited September 2004). This means that the measured molecular masses were overestimated for Cereclor^{TM} 60L and S52, and underestimated for Cereclor^{TM} 70L.

The GC-MS analysis of the SCCP and MCCP mixtures showed that, not only hexa- and heptachloro un- and dodecanes are predominant isomers as reported by Tomy *et al.* (1998). Mixtures with lower chlorine contents had a higher amount of C_{11}-, C_{12}-, C_{14}- and C_{15}- components with 5-7 chlorine atoms, those with higher chlorine contents had higher chlorinated compounds as main components (> Cl_7).

4.3.2 CACI-LRMS

CACI-MS gave a better agreement between the calculated and specified chlorine content of CP mixtures. The deviations for technical CP mixtures ranged between 0-6% for SCCPs (mean 3±2%) and between 1-11% for MCCPs (mean 4±3%) (see Table 22). ECNI-MS gave significant different results (SCCP: 6±5% and MCCP: 9±7%, t-Test). CACI-MS underestimated the chlorine content in most cases. SCCP mixtures were dominated by un- and dodecanes with four to nine chlorine atoms depending on the chlorine content (see Table 22) and MCCPs by C_{14} and C_{15} compounds.

The different ionization techniques had no influence on the cluster membership (see Figure 9). Only a better separation of Cereclor^{TM} 70L (high chlorine content) and Chloroparaffin 45fl (higher abundance of C_{15} and C_{16} compounds) was observed for CACI-MS.

Table 22. Composition of technical SCCP and MCCP mixtures obtained by HRGC-CACI-LRMS. Information is given about the specified and calculated average chlorine content [% Cl], the calculated average molecular mass [g/mol], the distribution of C_{10-13} and C_{14-16} congeners with 4-10 chlorine atoms [%].

Mixture	Chlorine content [% Cl]		Molecular mass [/mol]	Distribution [%]				Main components	
	specified	calculated	calculated	C_{10}	C_{11}	C_{12}	C_{13}	$C_{11}Cl_x$	$C_{12}Cl_x$
SCCP 51.5% Cl [a]	51.5	53.2±0.1	342±2	7±1	34±2	38±1	22 ±2	4/5	4/5
SCCP 55.5% Cl [a]	55.5	55.4±0.1	358±1	8±1	38±1	36±1	18 ±1	5/6	5/6
SCCP 63.0% Cl [b]	63.0	59.8±0.4	394±3	11±1	40±4	32±3	17 ±1	6/7	6/7
Hordalub 17	49.0	51.0	332	7	34	34	25	4/5	4/5
Hordalub 80	56.0	55.2	358	9	37	34	19	5/6	5/6
Cereclor™ 60L	59.0	57.2	377	12	26	37	25	6/7	6/7
Hordalub 500	62.0	59.5	387	10	47	31	12	6/7	6/7
Cereclor™ 70L	69.0	65	461	8	24	35	33	[b]	8/9
				C_{14}	C_{15}	C_{16}	C_{17}	$C_{14}Cl_x$	$C_{15}Cl_x$
MCCP 47% Cl [a]	47.0	45.4±0.1	364±1	73±1	24±1	3±1	n.a.	4/5	4/5
MCCP 52% Cl [a]	52.0	50.6±0.4	400±3	76±1	21±1	3±1	n.a.	5/6	5/6
MCCP 57% Cl [a]	57.0	53.7±0.6	425±6	73±1	21±2	6±1	n.a.	6/7	6/7
Chlorparaffin 40fl	41.0	45.7	370	64	27	9	n.a.	4/5	4/5
Chlorparaffin 45fl	46.0	45.6	388	16	47	38	n.a.	4/5	4/5
Hordalub 80 EM	49.0	49.0	400	49	32	19	n.a.	5/6	5/6
Cloparin 50	51.0	49.5	398	62	25	13	n.a.	5/6	5/6
Cereclor™ S52	52.0	50.8	405	71	16	13	n.a.	5/6	5/6
Hordaflex SP	56.0	52.8	437	36	29	34	n.a.	6/7	6/7

[a] mean of 4-5 measurements at different days; n.a. not analysed; [b] $C_{13}Cl_{9/10}$ are main components

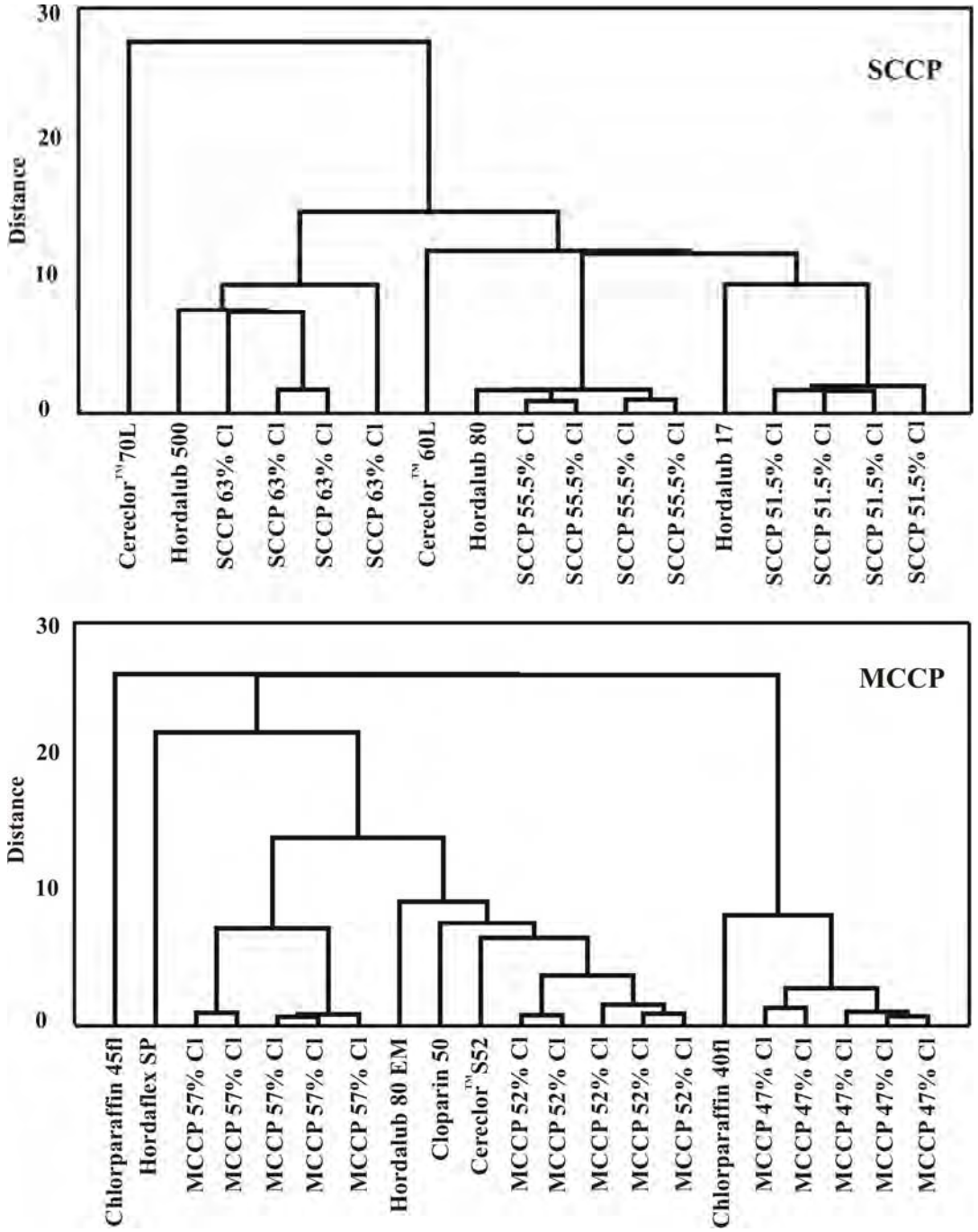

Figure 9. Complete linkage dendrogramm (Euclidian distance) of technical SCCP and MCCP mixtures (for data see Table 22). Homologue and congener group composition was obtained by HRGC-CACI-LRMS.

4.3.3 Comparison of congener and homologue patterns obtained by ECNI-MS and CACI-MS

The congener patterns of 17 technical CP mixtures were determined by ECNI-MS and CACI-MS. Table 23 lists the average chlorine contents and molar masses calculated according to an earlier published procedure (Tomy *et al.* 1997). ECNI-MS always overestimated the chlorine content except for Cereclor™ 70L. CACI-MS underestimated it in most cases.

Table 23. Comparison of the calculated average molecular masses [g/mol] and average chlorine contents [% Cl] of technical SCCP and MCCP mixtures determined by HRGC-ECNI-LRMS and HRGC-CACI-LRMS.

Technical mixture	Molecular mass [g/mol]		Ratio ECNI/CACI	Chlorine content [% Cl]		Ratio ECNI/CACI
	ECNI	CACI		ECNI	CACI	
C_{10-13}	**Cl_{5-10}**	**Cl_{4-10}**				
SCCP 51.5% Cl [a]	384±4	342±2	1.12	57.5±0.2	53.2±0.1	1.08
SCCP 55.5% Cl [a]	396±2	358±1	1.11	59.2±0.1	55.4±0.1	1.07
SCCP 63.0% Cl [a]	432±12	394±3	1.10	62.9±1.1	59.8±0.4	1.05
Hordalub 17	375	332	1.13	56.7	51.0	1.11
Hordalub 80	397	358	1.11	59.6	55.2	1.08
Cereclor™ 60L	414	377	1.10	61.1	57.2	1.07
Hordalub 500	425	387	1.10	63.2	59.5	1.06
Cereclor™ 70L	460	461	1.00	65.2	65.0	1.00
C_{14-16}						
MCCP 47.0% Cl [a]	413±4	364±1	1.13	52.2±0.3	45.4±0.1	1.15
MCCP 52.0% Cl [a]	443±1	400±3	1.11	55.7±0.1	50.6±0.4	1.10
MCCP 57.0% Cl [a]	466±4	425±6	1.10	57.5±0.2	53.7±0.6	1.07
Chlorparaffin 40fl	412	370	1.11	51.6	45.5	1.13
Chlorparaffin 45fl	430	388	1.11	51.1	45.6	1.12
Hordalub 80EM	438	400	1.10	53.7	49.0	1.10
Cloparin 50	439	398	1.10	54.4	49.5	1.10
Cereclor™ S52	450	405	1.11	56.0	50.8	1.10
Hordaflex SP	469	437	1.07	56.7	52.8	1.07
Mean±standard deviation			1.10±0.03			1.09±0.03

[a] Mean of 4-5 measurements

Consequently, the chlorine content ratio between ECNI-MS and CACI-MS varied between 1.00 and 1.13 (1.09±0.03) for all investigated technical mixtures. A similar ratio was also obtained for the calculated average molar masses (range between 1.00-1.13, average 1.10±0.03).

The detection of lower chlorinated compounds by CACI-MS changed the congener and homologue group patterns (see Figure 10). The ECNI-MS congener pattern of the technical SCCP mixture (55.5% Cl) was dominated by Cl_{6-7} congeners compared to CACI-MS, where Cl_{5-6} compounds are most abundant. Similarly, a shift from Cl_{7-8} to Cl_{6-7} was observed for a MCCP mixture (57.0% Cl). The same was observed for technical CP mixtures (Hordalub 500 and Chlorparaffin 40fl from Hoechst AG, Germany). In general, the main congeners of a given C-chain have one Cl more when detected by ECNI-MS. Also the pattern for each carbon chain length shifts to the next higher chlorinated congener for ECNI-MS.

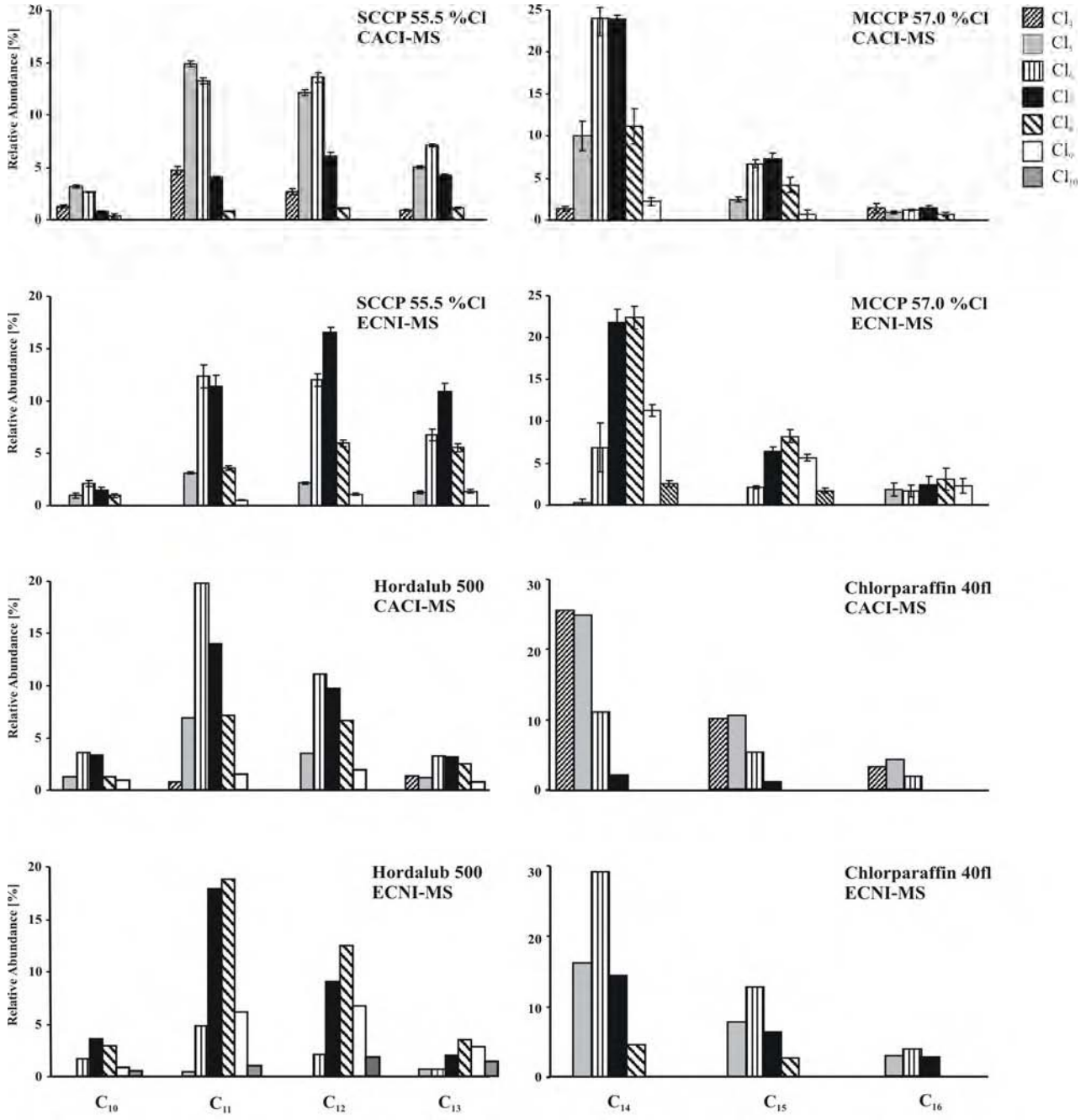

Figure 10. Comparison of SCCP and MCCP congener group patterns obtained by CACI-MS and ECNI-MS. Two technical mixtures (55.5 and 57% Cl) as well mixtures from Hoechst, Germany (Hordalub 500 and Chlorparaffin 40fl) were analysed. Error bars for 4-5 parallels are given.

4.3.4 GC×GC-LRMS

In recent years the analysis of complex substance classes such as toxaphenes or chloroparaffins has become more and more important in environmental analysis. Conventional single-column gas

chromatography does not allow a complete separation due to the large number of single compounds. A significant advance in chromatographic separations was made with the application of comprehensive two-dimensional GC. Separation in two dimensions is more powerful than in one. Therefore, GC×GC can handle much more complex mixtures (Korytar *et al.* 2005a).

Figure 11 shows the structure arranged according to the number of chlorine atoms with four separated parallel peak groups in the chromatogram of a polychlorinated decane mixture with an average chlorine content of 50%. Separation of decane, undecane, dodecane and tridecane mixtures with chlorine contents between 50 and 70% showed the presence of congeners with 5-10 chlorine atoms (Figure 11). Mainly congeners with 5-8 chlorine atoms were detected for mixtures with 50% Cl independently from the carbon chain length. Mixtures with 60% Cl showed the presence of congeners with 6-9 chlorine atoms and mixtures with 70% Cl congeners with 7-10 chlorine atoms. These results were also confirmed by single-column GC-ECNI-MS (see Table 24).

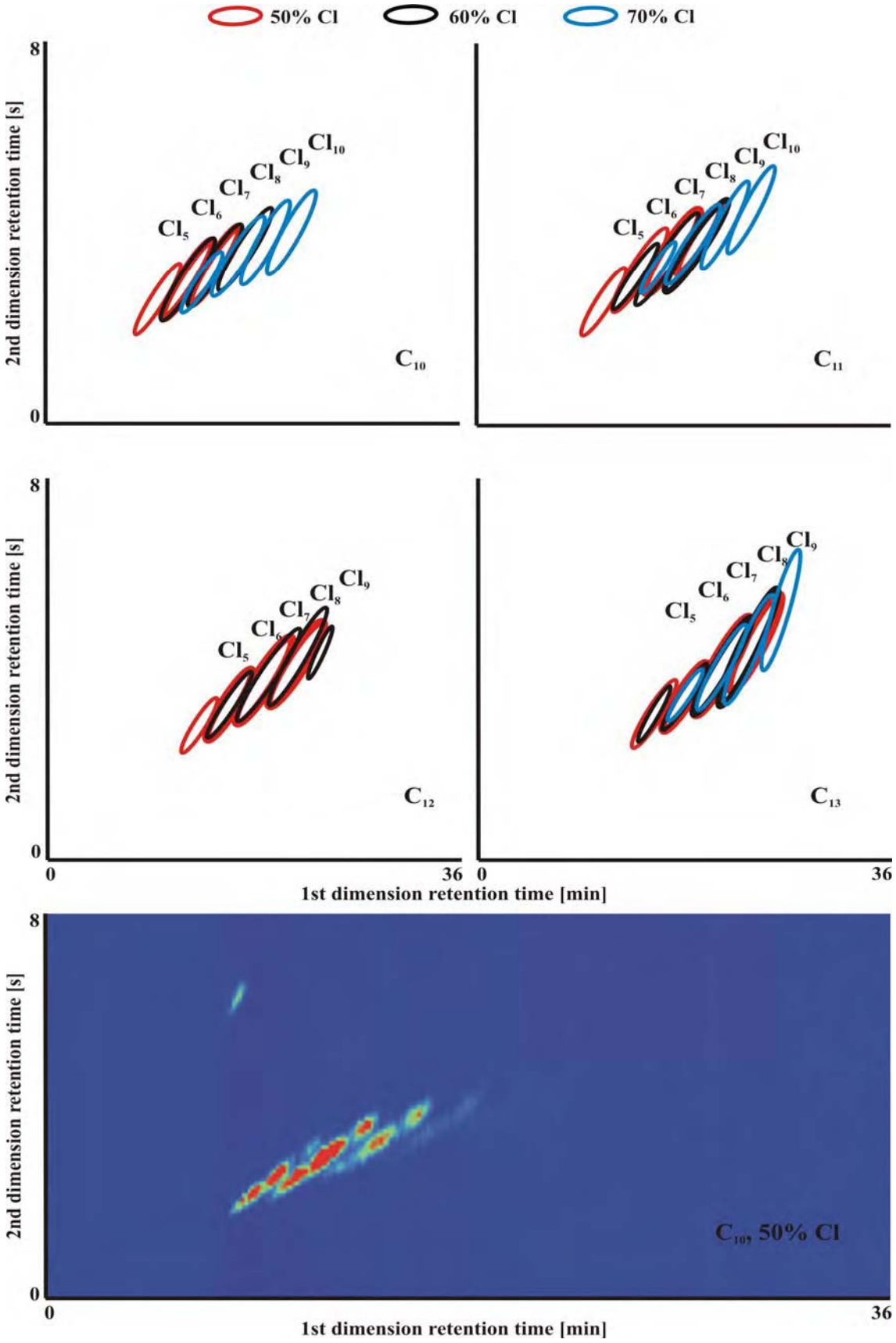

Figure 11. GC×GC-ECNI-MS chromatograms (scan mode) of polychlorinated decanes, undecanes, dodecanes and tridecanes with average chlorine contents of 50, 60 and 70%. Red, black and blue lines indicate the observed peak groups or bands of the different chlorine contents.

Table 24. Relative abundance of C_{10}, C_{11}, C_{12} and C_{13} congeners [%] of CPs with defined chain length obtained by HRGC-ECNI-LRMS (Varian 1200L). The specified and calculated chlorine content [% Cl] is also given.

	Chlorine content [% Cl] specified	Chlorine content [% Cl] calculated	Relative abundance [%]					
			Cl_5	Cl_6	Cl_7	Cl_8	Cl_9	Cl_{10}
C_{10}	50	61.1	23	47	22	5	3	0
	60	64.4	2	24	47	23	4	0
	70	69.0	0	3	11	29	41	16
C_{11}	50	58.4	10	40	37	11	2	0
	60	60.0	2	19	42	28	8	1
	70	64.4	0	2	10	26	39	23
C_{12}	50	58.8	8	34	38	17	3	1
	60	61.2	2	15	38	32	11	2
C_{13}	50	57.7	5	26	40	23	6	0
	60	60.3	1	10	29	38	18	4

SCCPs are a mixture of decanes, undecanes, dodecanes and tridecanes. The overlayed chromatogram of the different chain lengths and number of chlorine atoms is shown in Figure 12. The observation was that the longer chain CPs had higher retention times in the first dimension due to increased boiling points. Longer chain CPs had lower second dimension retention times within the same diagonal band.

CP compounds having the same sum of carbon and chlorine atoms were in the same diagonal peak group. For example, $C_{10}Cl_8$, $C_{11}Cl_7$, $C_{12}Cl_6$ and $C_{13}Cl_5$ are along the same line (sum of carbon and chlorine atoms 18). C_{10} mixtures with 60 and 70% Cl showed the presence of congeners with eight to ten chlorine atoms and an overlap with penta-, hexa- and heptachlorinated tridecanes. The ECNI mass spectra of CPs contain the three main ions $[M\text{-}HCl]^-$, $[M\text{-}Cl]^-$, and $[M+Cl]^-$ with structure dependent relative abundances. The relative abundance of the adduct ion is higher for congeners with four and five chlorine atoms than for higher chlorinated ones. SCCP congeners can cause mass overlap. For example, mass *m/z* 327 can be formed by a chlorine adduct of a $C_{11}H_{20}Cl_4$ congener or by a loss of chlorine from a $C_{11}H_{18}Cl_6$ congener. However, the separation by GC×GC solves this

problem. Both congeners can be found in different peak bands due to the different sum of carbon and chlorine atoms (15 vs. 17, Figure 12)

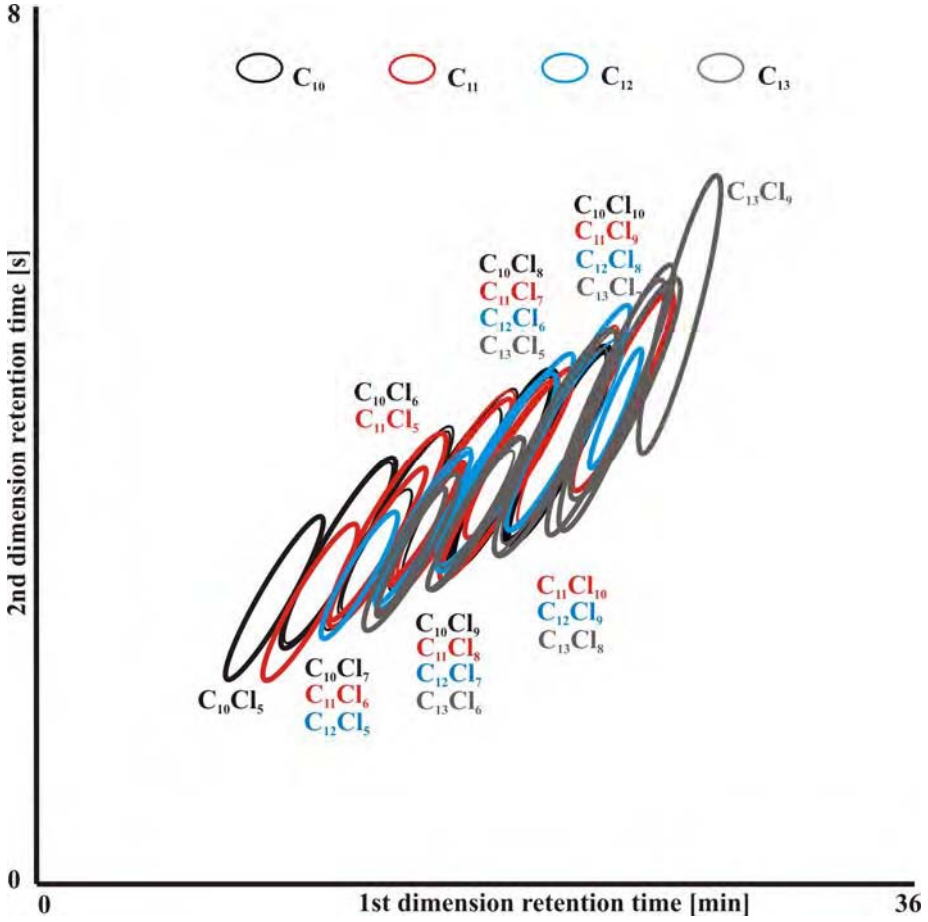

Figure 12. Overlay of GC×GC-ECNI-MS chromatograms of decanes, undecanes, dodecanes and tridecanes with chlorine contents between 50 and 70%. Colours indicate the different carbon chain lengths.

Studies with MCCP mixtures to confirm SCCP results were not possible, since C_{14}, C_{15}, C_{16} and C_{17}-MCCP mixtures with different chlorine contents are not commercially available. The chromatograms of MCCP mixtures with 47, 52 and 57% Cl showed the separation in peak bands as observed for the SCCPs (see Figure 13). MCCPs had lower second retention times. Furthermore, MCCP congeners are separated according to their sum of chlorine and carbon atoms as shown for SCCPs. However, a separation of SCCPs and MCCPs is not possible.

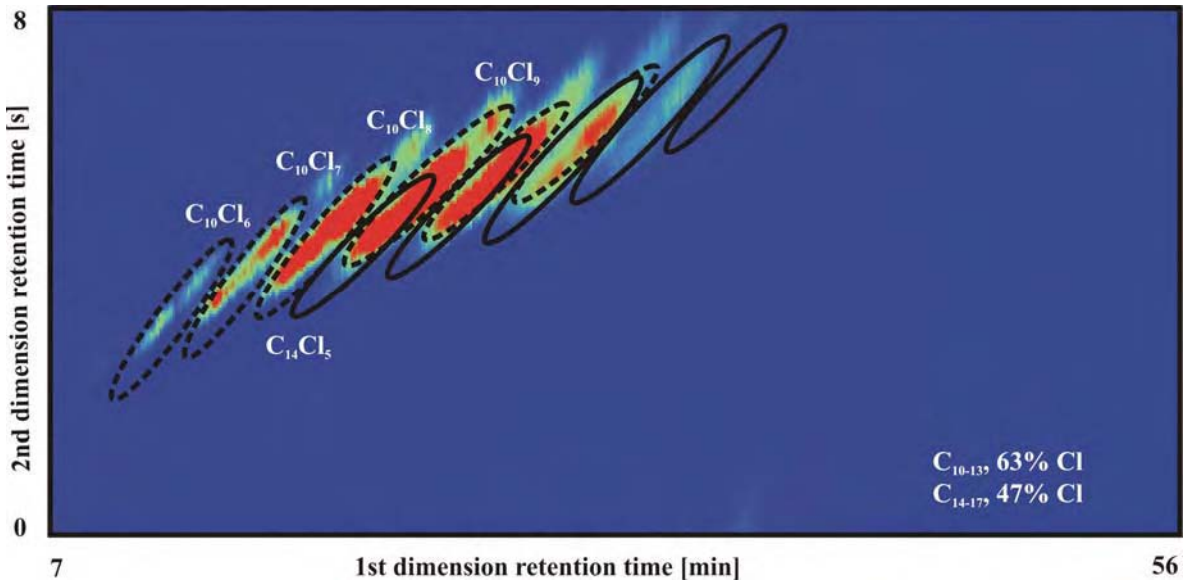

Figure 13. GC×GC-ECNI-MS (scan mode) chromatogram of a 1:1 mixture of a SCCP solution with 63% chlorine content and a MCCP solution with 47% chlorine content. SCCP peak bands are marked with a solid line and those of MCCPs with a dotted line.

The determination of minor quantities of C_{16} and C_{17} congeners in the presence of high levels of C_{11} and C_{12} congeners is not possible by ECNI-MS due to mass overlap. The most abundant $[M\text{-}Cl]^-$ isotopes of SCCP congeners with 7 to 9 chlorine atoms overlap with MCCPs with five carbon atoms more and two chlorine less (for instance, $C_{11}H_{16}Cl_8$ and $C_{16}H_{27}Cl_6$). An overestimation of the MCCP concentration is the result. Figure 14 shows the GC×GC-ECNI-MS chromatograms of the $[M\text{-}Cl]^-$ ions of C_{16} and C_{17} congeners with 5 to 10 chlorine atoms of SCCP solutions and of the technical MCCP mixture Chlorparaffin 45fl. The elution area of the SCCP congeners is marked with solid lines in the chromatogram of the technical MCCP mixture Chlorparaffin 45fl. Differentiation between the MCCP and SCCP congeners is possible due to their different retention behaviour. Quantification of minor C_{16} and C_{17} congeners in the presence of SCCPs is possible.

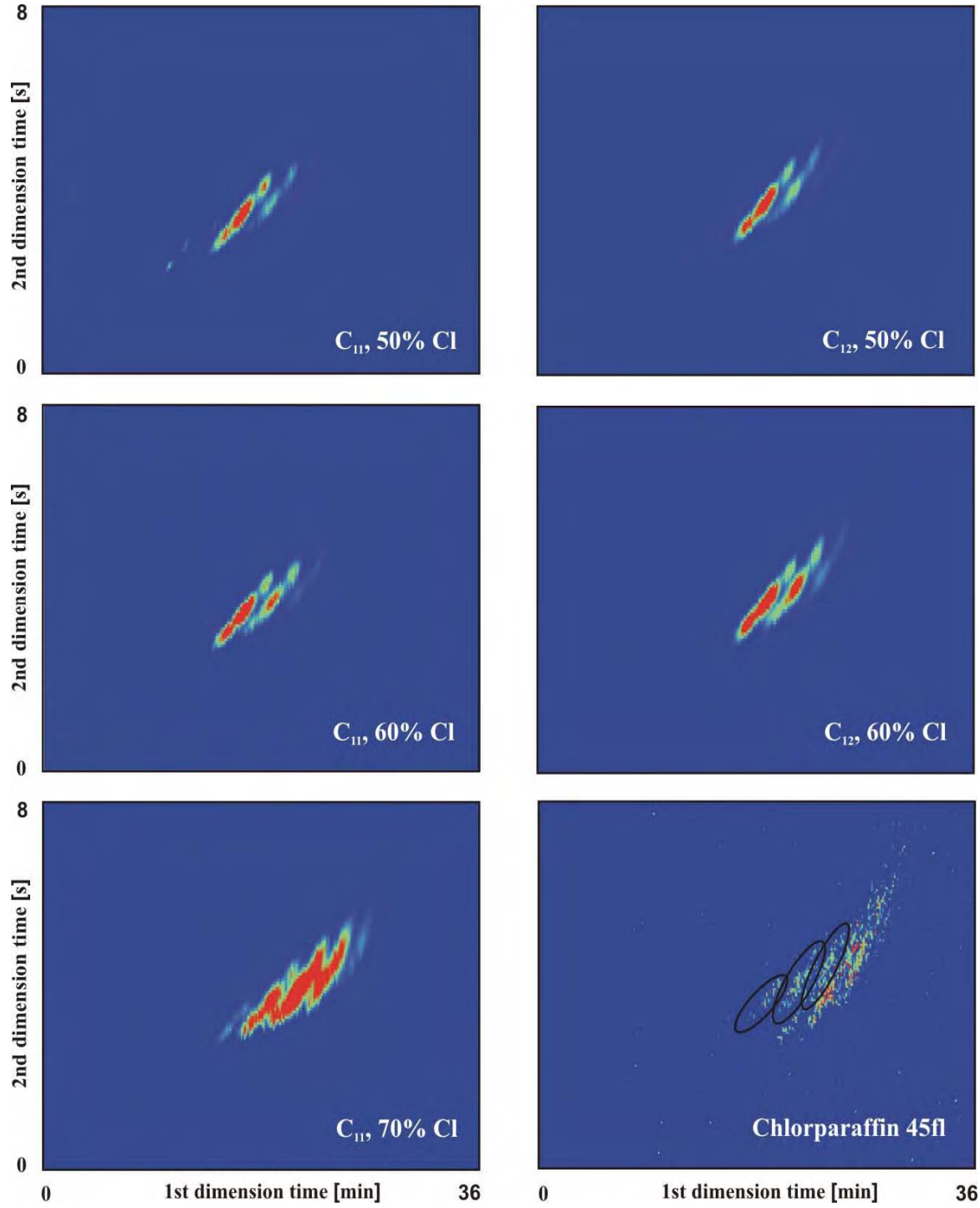

Figure 14. GC×GC-ECNI-MS chromatograms of the $[M\text{-}Cl]^-$ ions of C_{16} and C_{17} congeners with 5 to 10 chlorine atoms of SCCP solutions and of the technical MCCP mixture Chlorparaffin 45fl. Peak bands of SCCPs are marked with a solid line in the chromatogram of Chlorparaffin 45fl.

Technical SCCP and MCCP mixtures were also investigated. Figure 15 shows the chromatograms of mixtures with different chlorine contents. An increase of the chlorine content showed the

presence of higher chlorinated and the absence of lower chlorinated congeners which, were well separated into peak bands. Mixtures showed differences in elution patterns, which can be used for differentiation between different chlorine contents, chain lengths as well as producers.

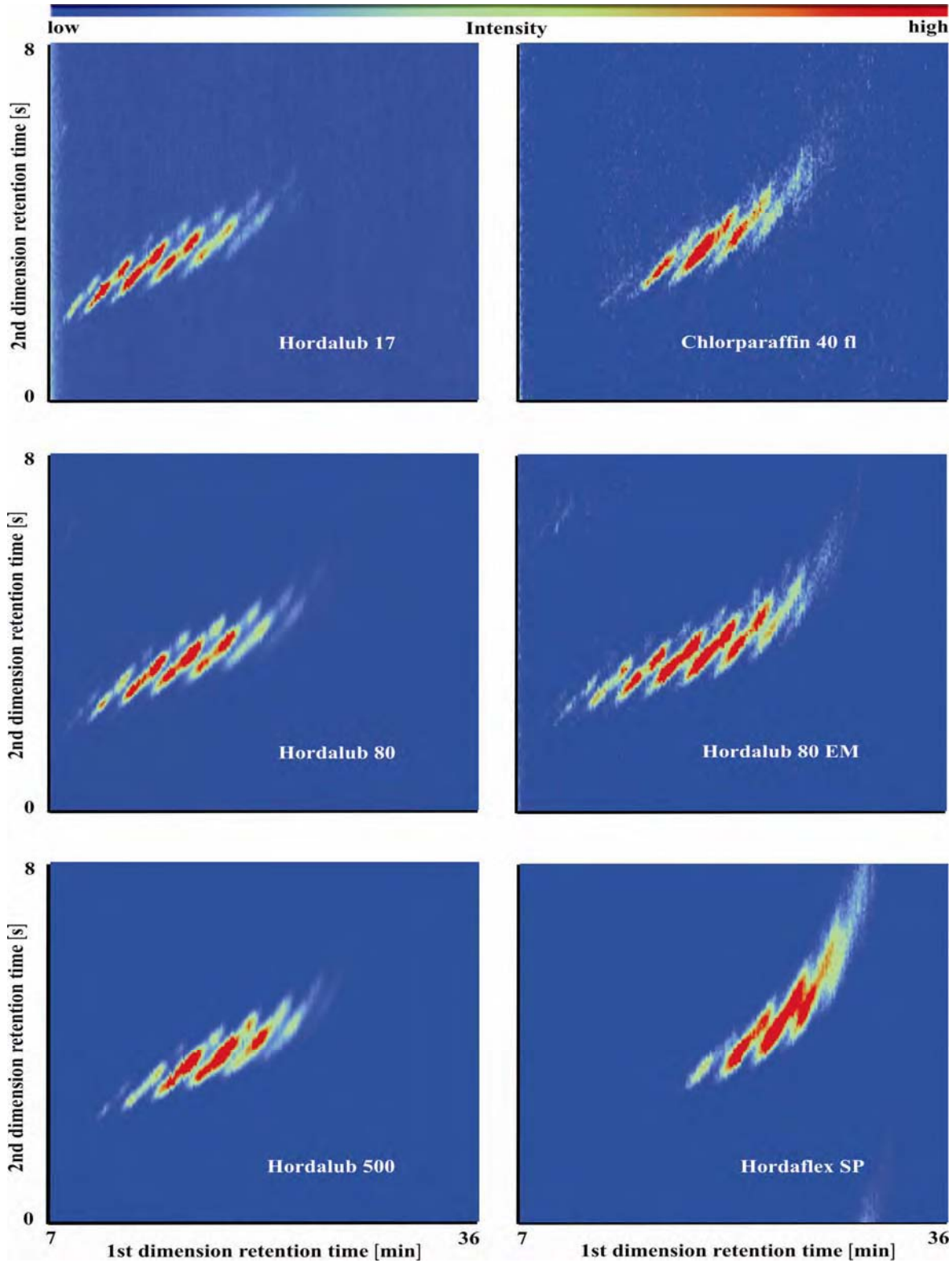

Figure 15. GC×GC-ECNI-MS (scan mode) chromatograms of technical SCCP (left side) and MCCP (right side) mixtures with different chlorine contents (SCCP: Hordalub 17, 80 and 500 with 40, 56 and 62% Cl; MCCP: Chlorparaffin 40fl, Hordalub 80 EM and Hordaflex SP with 41, 49 and 56% Cl).

4.3.5 NMR

The actual substitution pattern of the carbon chain is unknown. So far, only few NMR studies have been carried out to study the structure of chlorinated paraffins (Gusev *et al.* 1968, Panzel and Ballschmiter 1974). The absence of CCl_2 groups was shown for chlorinated *n*-hexadecanes with a chlorine content < 60% (only $(CHCl)_n$ groups). Also CCl_2 groups were present for higher degrees of chlorination (Gusev *et al.* 1968). Panzel et al. (1974) showed the differentiation of CP mixtures according to chain lengths and degree of chlorination by NMR.

Figure 16 shows the HSQC spectra of SCCP mixtures with different chlorine contents. The differences in the spectra of Hordalub 17 and 80 were small, but deviated from that of Hordalub 500. Signal overlap of thousands of single compounds in the mixture made the interpretation of the spectra rather complex. Therefore, 1,2-dichlorobutane and 1,3-dichlorobutane were used as model compounds to confirm some structure elements. The spectra were divided into nine groups and for each group a structure was proposed (see Figure 16 and Table 25). The number of carbon atoms only bound to hydrogen decreased with increasing chlorine content.

However, the influence of the chlorine substitution of the carbon chain on physical-chemical properties is difficult to interpret. Only few single CP compounds are available for such studies. But CP mixtures contain several thousands of single compounds. Therefore, the possibility of synergistic and antagonistic effects is given for CP mixtures.

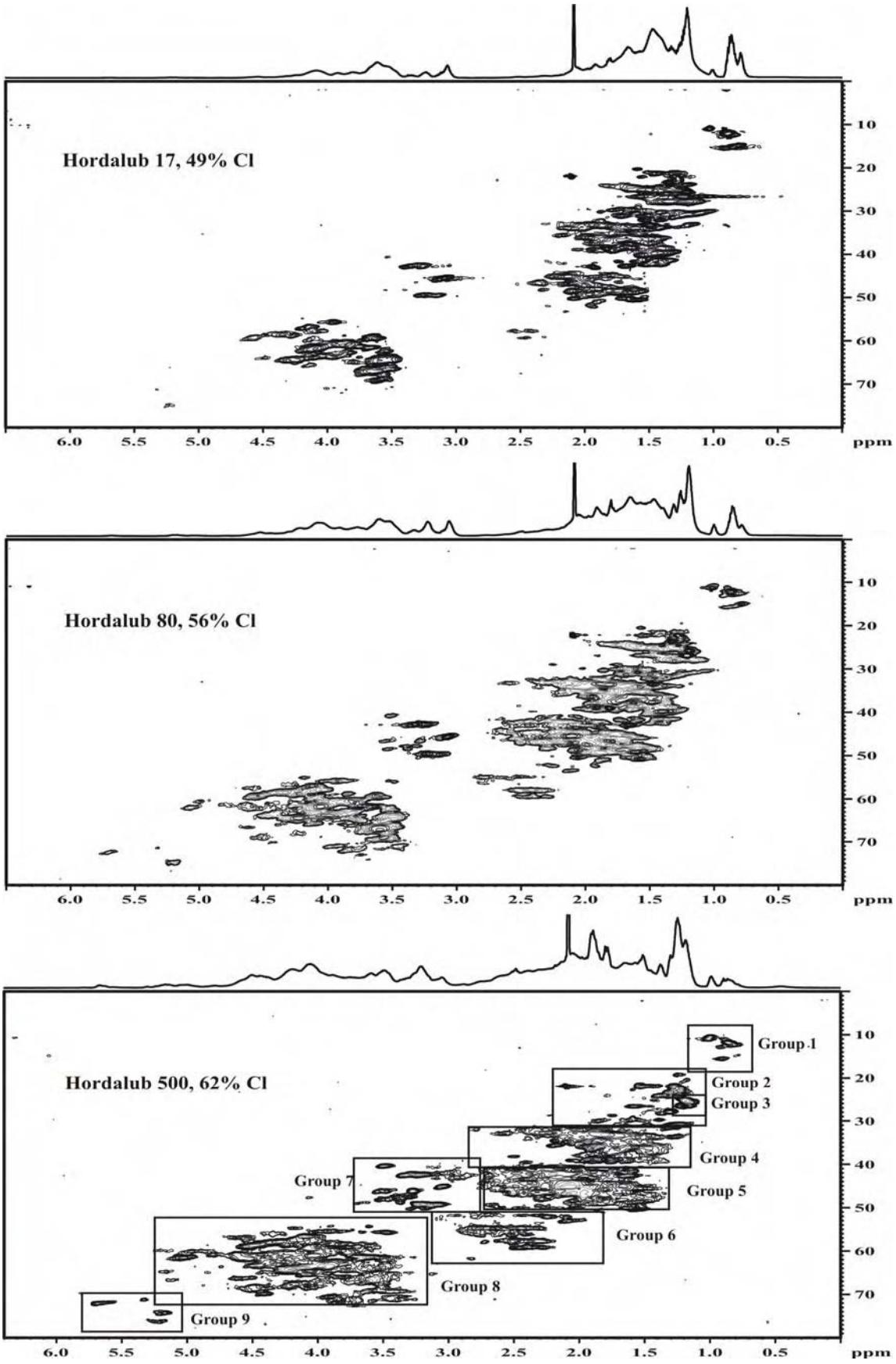

Figure 16. HSQC spectra of technical SCCP mixtures with different chlorine content dissolved in d_8-toluene.

Table 25. Relative abundances [%] of structure elements in technical SCCP mixtures.

		Relative abundance [%]		
Group	**Structure**	**Hordalub 17**	**Hordalub 80**	**Hordalub 500**
1	CH_3-CH_2-	6	3	2
2	CH_3-CH_2-CCl-	16	13	11
3	CH_3-ClCH-	6	5	2
4	-ClC-CH_2-ClC-	29	26	17
5	$ClCH_2$-CH_2-CH/Cl-	17	21	24
6	$ClCH_2$-Cl_2C-	1	2	5
7	$ClCH_2$-CH-	5	7	8
8	-C-ClCH-C-	19	24	30
9	Cl_2CH-	1	1	1

The flame retardant properties increase with increasing chlorine content. The use of CPs as flame retardant additives based on the release of large amounts of hydrogen chloride at high temperatures, which is not only non-flammable but can also prevent the fire spreading (GDCh Advisory Committee on Existing Chemicals of Environmental Relevance 1992). Bioconcentration potential decreases with increasing molecular weight (chlorine content and carbon chain length). Increasing chlorine content inhibits degradation. Differences in bioaccumulation parameters between CPs with the same molecular formular but different Cl positioning were observed (Fisk *et al.* 1998).

4.4 Chloroparaffin concentrations, congener and homologue patterns in sediments and suspended particular matter

4.4.1 Screening with EI-MS/MS

Total CP concentrations in sediments determined by EI-MS/MS are given in Table 26. They were between 5 and 499 ng/g dry weight (d.w.). The differences were small between the quantification based on a SCCP or MCCP technical mixtures with similar chlorine content (< 15% deviation).

Except for sampling sites KS 8 and 11, total CP concentrations in the North Sea (German Bight) were lower than in the Baltic Sea (see also Figure 17). In general, the concentrations in the North Sea were too low for a determination of the congener and homologue patterns by ECNI-MS with few exceptions. The highest total CP concentrations were found for sample 710 (2002, Kieler Förde) in the Baltic Sea and for KS 11 (2004) in the North Sea. KS 11 is situated in the Elbe estuary and mainly infuenced by the river Elbe.

However, total CP concentrations related to the TOC content were in the same order of magnitude for North and Baltic Sea due to the high organic content of the Baltic Sea sediments (see Table 6). The highest total CP concentrations on TOC basis in the North Sea were found for UE 70 and WB 1 with 0.07 and 0.03% TOC. Sample ODER was the most contaminated sampling site on TOC basis in the Baltic Sea.

CP concentrations were in same order of magnitude (relative standard deviation < 20%) for different sampling years. However, also differences were also observed for 710 (Baltic Sea), KS 8 and 11 (North Sea). Total CP concentrations of 377 ng/g and 45 ng/g dry weight were determined in 2002 and 2004 for location 710 (see Figure 17). One explanation might be the large difference between the total organic carbon content for the two years. The concentration ratio of ca. 8.5 is similar to that of the TOC (2002: 5.3 %, 2004: 0.5%). CP concentrations based on TOC were in good agreement (9.4 and 7.7 μg/g TOC). The TOC content was a good marker for CP concentrations (excepted sample ODER, UE 67, UE 70, WB 1). Higher TOC levels indicated usually also higher CP levels. A linear correlation between the TOC and the CP concentrations could not be established for all marine sediment samples ($r^2 = 0.44$) and for those from the Baltic

Sea (r^2 = 0.28). However, a correlation was found for the North Sea sediments (r^2 = 0.79). All investigated sample sites were influenced by urban and rural sites.

Levels of C_{10}-C_{20} chloroparaffin in North Sea sediments published as early as in 1980 were < 0.5-50 ng/g for 3 sediment locations and between 25-125 ng/g d.w. (C_{10-24}) for two mud flats in the North Sea (Campbell and McConnell 1980, Greenpeace 1995). Results from 1995 also showed high concentrations of γ-HCH, p,p`-DDT, p,p`-DDE, p,p`-DDD as well as high levels of PCBs in Oder bottom sediments compared to sampling sites close to Warnemünde and in the Pomeranian Bay (Ciereszko 2002). Location KS 11 showed also high concentrations of hexachlorobenzene, polychlorinated biphenyls, DDT and hexachlorocyclohexanes in 1997 and 1998 (BLMP 2002) compared to other North Sea sites. CPs are in active production and widespread use, therefore, it is not surprising that they are present at much higher concentrations than other related families of persistent organic pollutants like PCBs (normally pg/g range; see also table 37), whose use has been extensively phased out.

Table 26. Total CP concentrations in North and Baltic Sea sediments (2001-2004) given in ng/g dry weight and on total organic carbon content basis [µg/g TOC]. Data were obtained by HRGC-EI-MS/MS. Quantification was carried out by quantification with a SCCP and MCCP standard (55.5% Cl respective 57.0% Cl).

	Amount [g]	Total CP [a] [ng/g d.w.]	Total CP [b] [ng/g d.w.]	Total CP [a] [µg/g TOC]	Total CP [b] [µg/g TOC]
Baltic Sea					
710 (2001)	4	262	211	8.4	6.8
710 (2002)	5	377	499	7.1	9.4
710 (2004)	10	45	37	9.4	7.7
715 (2001)	4	116	93	4.0	3.2
715 (2004)	10	83	68	2.7	2.2
718 (2001)	4	141	115	3.7	3.0
718 (2004)	10	232	176	6.4	4.8
721 (2001)	4	142	114	2.4	1.9
721 (2002)	5	108	122	2.1	2.3
721 (2004)	10	138	105	2.8	2.2
ECKFBU	10	158	124	3.9	3.1
ODER	10	75	59	83	66
RUDEN	10	136	107	4.8	3.8
North Sea					
KS 8 (2002)	30	14	13	4.1	4.9
KS 8 (2003) [c]	20	145	125	18	16
KS 8 (2004)	10	267	211	22	18
KS 11 (2002)	10	112	146	6.7	8.7
KS 11 (2003) [c]	10	98	77	8.9	7.0
KS 11 (2004)	5	355	290	14	12
BL 2	10	27	28	4.8	4.9
BL 4	30	8	9	3.7	4.3
UE 18	50	5	6	5.2	5.7
UE 28	50	9	9	9.1	8.6
ES 1 [c]	20	20	24	33	39
TI 13 [c]	20	15	18	21	25
UE 15 [c]	20	27	32	12	14
SSL [c]	10	n.a.	63 [d]	n.a.	2.3
UE 20 [c]	20	25	30	6.9	8.2
L 1 [c]	20	16	19	12	15
WB 5 [c]	20	16	18	3.4	4.6
UE 67 [c]	20	24	26	20	22
UE 70 [c]	20	33	40	47	57
WB 1 [c]	20	18	13	60	42

[a] Quantification with a SCCP (55.5% Cl) and [b] a MCCP (57.0% Cl) standard; [c] average of two CID; [d] standard addition of MCCP with 57.0% Cl; n.a. not analyzed

Higher CP concentrations in the Baltic Sea compared to the North Sea were expected. The Baltic Sea is almost completely confined by landmasses of the European continent (WWF 2005). Exchange of saltwater with the North Sea is limited. Water exchange with the open ocean only occurs through the strait between Denmark and Sweden. The water remains in the sea for 25-30 years. Furthermore, large amounts of fresh water enter the Baltic Sea from over 200 rivers (e.g. Oder, Neva). Therefore, contaminants of a huge catchment area are "trapped" in a large brackish water system (average depth of 23-50 m). The dilution factor for hazardous substances is smaller compared to other seas. High sedimentation rates compared to that of oceans lead to an increased input of particle-bound contaminants to sediments (WWF 2005).

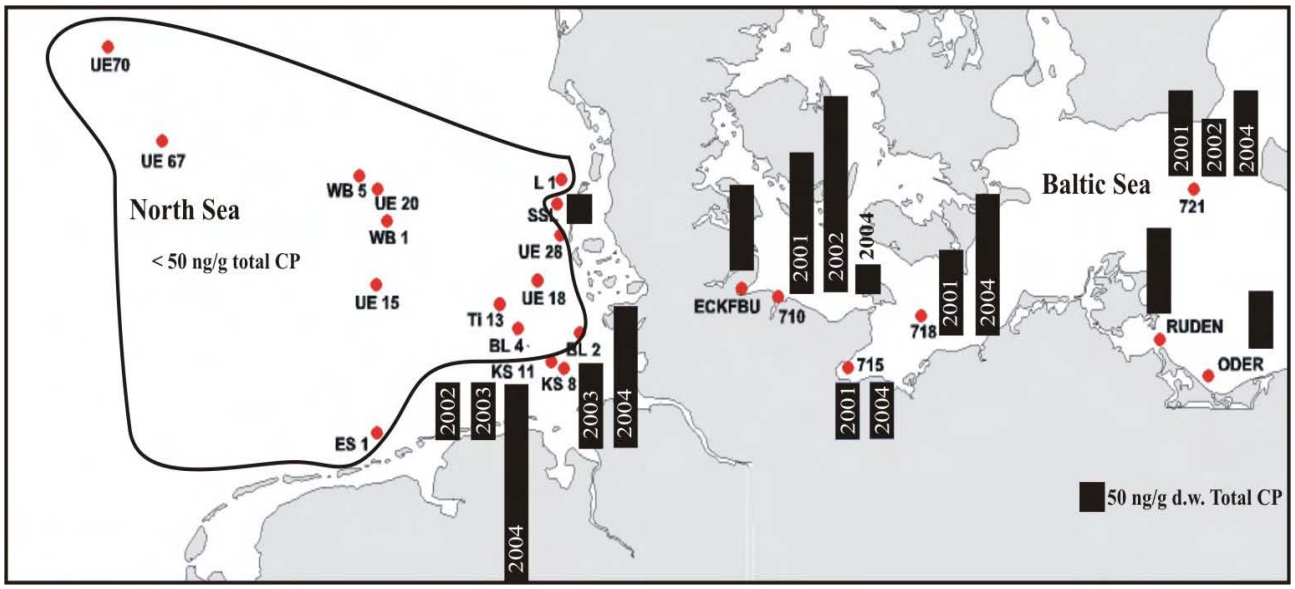

Figure 17. Sampling sites and total CP concentrations [ng/g dry weight] in the North and Baltic Sea (2001-2004) obtained by HRGC-EI-MS/MS (quantification standard: SCCP mixture with 55.5% Cl).

Total CP levels were also determined for freshwater sediments and suspended particular matter (SPM) from the Seine estuary, harbours of Hamburg and Tromsø and from Rhine and Neckar. The concentrations varied between 70 and 163 ng/g d.w. for freshwater sediments and between 127-669 ng/g d.w. for SPM (see Table 27). The CP concentrations on TOC basis were in the same range as

the results from the North and Baltic Sea sediments. No correlation existed between the TOC content and the determined CP concentrations.

CP levels of the different sampling sites at the Seine estuary, Hamburg harbour as well as Neckar and Rhine were in the same order of magnitude as the levels in the sea sediments (see Table 26). The sampling sites in Neckar, Rhine and Hamburg harbour can be characterized as follows:

- Neckar (Feudenheim at km 8 and Poppenweiler at km 165): catchment area of 14'000 km^2; around 5 million inhabitants; conurbation of Stuttgart, Heilbronn and Heidelberg; mainly metal working and car industry; input of 587 local waste water treatment plants (WWTP) (Lehmann 2005).
- Rhine (Iffezheim at km 334): downstream of Rheinfelden, Basel and Mulhouse-Chalampé (mainly chemical and pharmaceuticals industry); less input of local WWTPs compared to Neckar (Lehmann 2005).
- Hamburg harbour: influence of river Elbe (high pollution from Czech Republic and former GDR), North Sea (50 million m^3 water per tide) and town Hamburg; high amount of sand and mud (2 million m^3 per year) transported by Elbe and North Sea; mainly metal pollution (Freie und Hansestadt Hamburg 2000, Lueschow 2004).

Sample Hamburg 1 was mud from Hamburg harbour, Hamburg 2 sediment from polluted harbour area influenced by the former GDR and Hamburg 3 fresh harbour sediment (influence by the Unterelbe).

Table 27. Total CP concentrations in river sediments, harbour areas and suspended particular matter given in ng/g dry weight and on total organic carbon content basis [µg/g TOC]. Data were obtained by HRGC-EI-MS/MS. Quantification was carried out by standard addition or by a MCCP standard.

Sample	**Total CP [a] [ng/g d.w.]**	**Total CP [b] [ng/g d.w.]**	**Total CP [a] [µg/g TOC]**	**Total CP [b] [µg/g TOC]**
Sediment				
Seine estuary 1	163	142	10	8.9
Seine estuary 2	70	n.a.	99	
Seine estuary 3	97	76	12	10
Hamburg 1 (harbour)	156	n.a.	5.0	
Hamburg 2 (harbour)	102	n.a.	3.4	
Hamburg 3 (harbour)	107	98	4.9	4.5
	112	n.a.	5.1	
Tromsø 1 (harbour)	104	n.a.	5.8	
Tromsø 2 (harbour)	89	n.a.	3.7	
Suspended particular matter				
Elbe	235	155/223 [c]	3.4	2.0
	226	n.a.	3.2	
North Sea 1	195	n.a.	3.5	
North Sea 2	204	n.a.	1.9	
Neckar 1				
August 2002	195	336/320 [c]	3.4	4.4
September 2002	n.a.	186/177 [c]		4.9
November 2002	n.a.	331/270 [c]		5.6
December 2002	n.a.	631/509 [c]		9.7
Neckar 2				
August 2002	669	[d]	20	
September 2002	n.a.	292		9.1
Rhine				
August 2002	138		2.7	
September 2002	n.a.	127		6.7
December 2002	n.a.	310		7.0

[a] standard addition of three times 200 ng absolute MCCP with 57% Cl relative to ε-HCH; [b] quantification standard MCCP with 57% Cl; [c] results were determined on two different days, parallel measurements each day ; [d] recovery ISTD < 50%; n.a. not analysed

Concentrations were either determined by standard addition (three times 200 ng total MCCP 57% Cl) or by internal standard quantification. Results obtained by both methods were in good agreement (accuracy < 27%, 5 samples). Samples were analyzed in parallel by EI-MS/MS.

Measurements on different days showed deviations < 18%. The recovery of the internal standard ^{13}C-*trans*-chlordane was always > 70%.

Own results were in good agreement with former published results. Levels of total chlorinated paraffin (SCCP, MCCP and LCCP) have been determined in estuarine sediments from Western Europe. The mean total level (SCCP, MCCP and LCCP) in the sediment fraction < 63 µm in the Mersey and Seine estuaries was 5.5 ng/g d.w. (European Chemicals Bureau 2002). Total CP concentrations of 93-98 ng/g, 193-200 ng/g and 205-288 ng/g d.w. were determined for Rhine sediments at kilometre 141, 152 and near the German-Dutch border (World Health Organization 1996). Levels for the river Elbe at two sites in Hamburg were in the same order of magnitude (146-255 ng/g d.w.). The Outer Alster (Hamburg) showed a level of around 400 ng/g. A CP level (C_{10-24}) of 42 ng/g d.w. was determined for Hamburg harbour (Greenpeace 1995).

4.4.2 Quantification by ECNI-LRMS

Figure 18 shows the SCCP and MCCP levels for eleven sediment samples from the North and Baltic Sea obtained by ECNI-MS. The quantification was performed according to the method described by Reth *et al.* (2005). SCCP and MCCPs could be detected in all marine samples. The SCCP concentrations varied between 8-63 ng/g d.w. (see Table 28). MCCP concentrations between 22 and 140 ng/g d.w. were determined. Levels of SCCPs in river sediments and SPM were between 21-144 ng/g and for MCCPs between 24 and 153 ng/g d.w.

MCCP concentrations were highest in all samples from the North and Baltic (ratio MCCP/SCCP 1.1-3.2, Table 28). Higher amounts of MCCPs compared to SCCPs were also found in all

investigated freshwater sediments and suspended particular matter samples (ratio MCCP/SCCP 1.4-5.2) except for sample Seine Estuary 2.

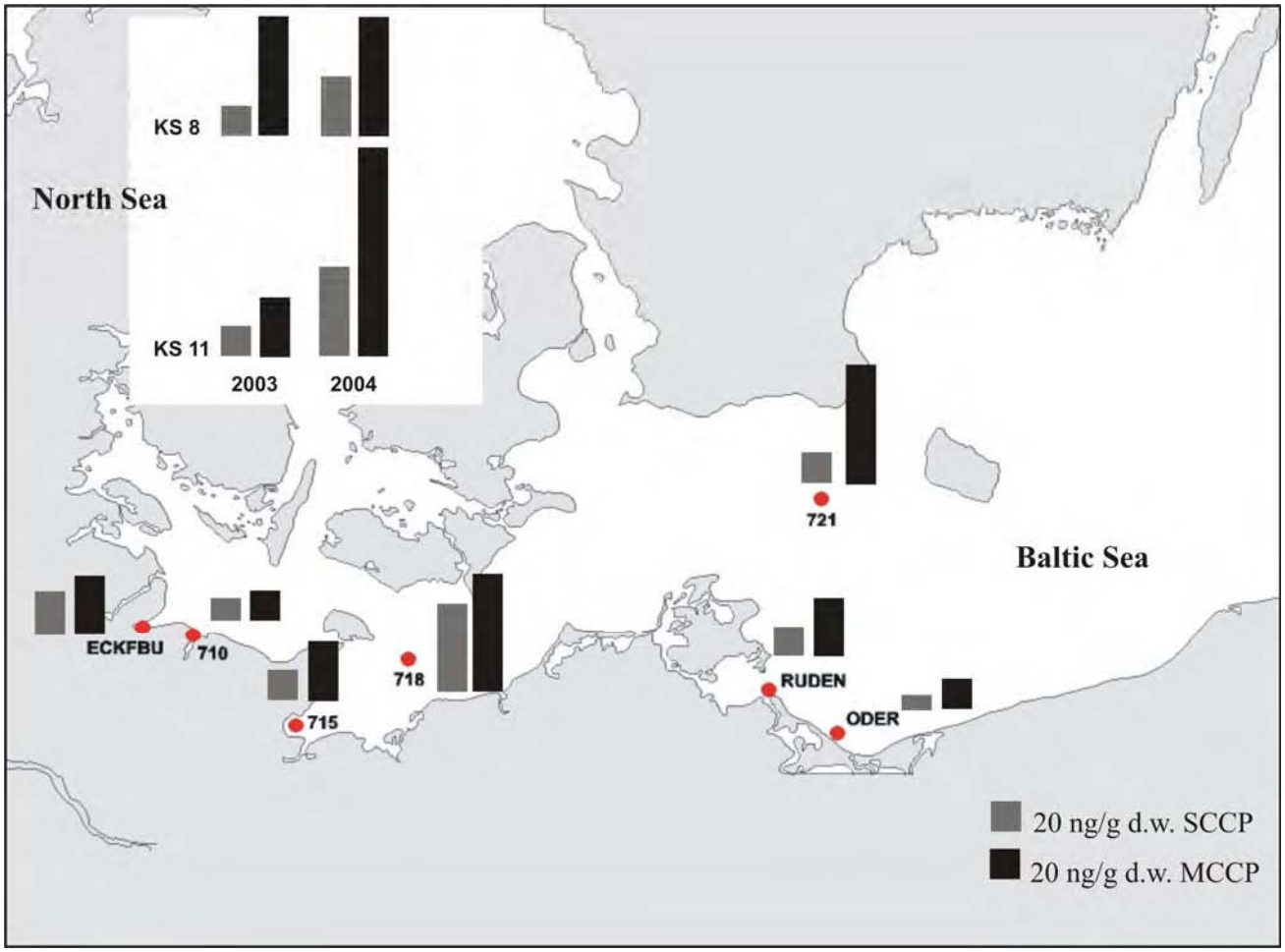

Figure 18. Map of sampling sites and SCCP and MCCP concentrations [ng/g dry weight] determined by HRGC-ECNI-LRMS in selected sediment samples from the North and Baltic Sea (2003-2004).

Table 28. SCCP and MCCP concentrations [ng/g dry weight] in marine and freshwater sediments as well as in suspended particular matter. The ratio of MCCP and SCCP concentrations is given. Data were obtained by ECNI-MS (quantification according to Reth *et al.* 2005).

Sample	SCCP (C_{10-13}) [a]	MCCP (C_{14-15}) [a]	S+MCCP (C_{10-15})	MCCP/SCCP
	[ng/g dry weight]			
North Sea				
KS 8 (2003)	27	87	114	3.2
KS 8 (2004)	43	48	91	1.1
KS 11 (2003)	13	34	47	2.6
KS 11 (2004)	63	149	212	2.4
Baltic Sea				
710 (2004)	15	23	38	1.5
715 (2004)	22	43	65	2.0
718 (2004)	53	85	138	1.6
721 (2004)	27	72	99	2.7
ODER	8	22	30	2.7
RUDEN	26	33	59	1.3
ECKFBU	31	39	70	1.3
Sediment				
Seine estuary 1	51	85	136	1.7
Seine estuary 2	41	24	65	0.6
Seine estuary 3	28	58	86	2.1
Hamburg 1	75	153	228	2.0
Hamburg 2	67	98	165	1.5
Hamburg 3	47	75	122	1.6
Tromsø 1	66	137	203	2.1
Tromsø 2	21	63	84	3.0
Suspended particular matter				
Elbe	46	116	162	2.5
Neckar 1				
August	81	124	205	1.5
September	53	85	138	1.6
November	78	112	190	1.4
December	79	407	486	5.2
Neckar 2				
September	144	215	359	1.5
Rhine				
August	47	124	171	2.6
September	22	54	76	2.5
December	43	124	167	2.9

[a] Quantification according to Reth *et al.* (2005); [b] recovery of ISTD < 50%

The results were in good agreement with earlier published results worldwide. SCCP levels in river sediments varied between 4.5-80.8 ng/g d.w. in the Czech Republic, between 0.25-3.26 µg/g in Spain and a average of 49 ng/g d.w. for Lake Ontario sediments (Marvin *et al.* 2003, Parera *et al.* 2004, Stejnarova *et al.* 2005). Kemmlein *et al.* (2002) reported MCCP concentrations between 1.1 and 16.4 µg/g for marine sediments, influenced by a CP manufacturer in Australia. In 1994, MCCP concentrations of < 10-370 ng/g were determined in German river sediments and 5 ng/g (C_{14-18}) in a surface sediment from Lake Zürich (World Health Organization 1996). MCCPs were thought to account for 13-78% of the total chlorinated paraffins present in mud samples from the North Sea, Rotterdam and Hamburg harbour (Greenpeace 1995). MCCP levels between 31 ng/g and 5576 ng/g d.w. were determined in the top layer of river sediments from the Czech Republic (Pribylova *et al.* 2005). Sampling locations were influenced by various industrial discharges.

Samples from Rotterdam and Hamburg harbour showed a MCCP to SCCP ratio of 1 and both mud samples from the North Sea ratios of 0.3 and around 6 (Greenpeace 1995). Similar observations were also made for German and Swiss river and lake sediments (World Health Organization 1996). There, MCCP levels were 2 to 10 times higher. The higher MCCP concentrations might be explained by the increased consumption due to the ban of SCCPs from different applications areas. Furthermore, MCCPs are known to be more adsorptive to surface areas and degrade more slowly than SCCPs.

4.4.2.1 Comparison of CP formular group patterns in marine sediments with freshwater sediments and suspended particular matter (SPM)

Chlorinated do- and tridecanes with 5-7 chlorine atoms were the main CP congeners in sediment samples from the North and Baltic Sea (see Table 29 and Figure 19). Freshwater and suspended

particular water samples were dominated by un- and dodecanes with six to eight chlorine atoms (see Table 30 and Figure 19). All investigated samples were dominated by chlorinated tetradecanes (MCCP) with 6-8 chlorine atoms (see Tables 29 and 30). No difference was observed for marine and freshwater sediments and SPM. C_{16} and C_{17} were not determined due to SCCP interferences (see chapter introduction).

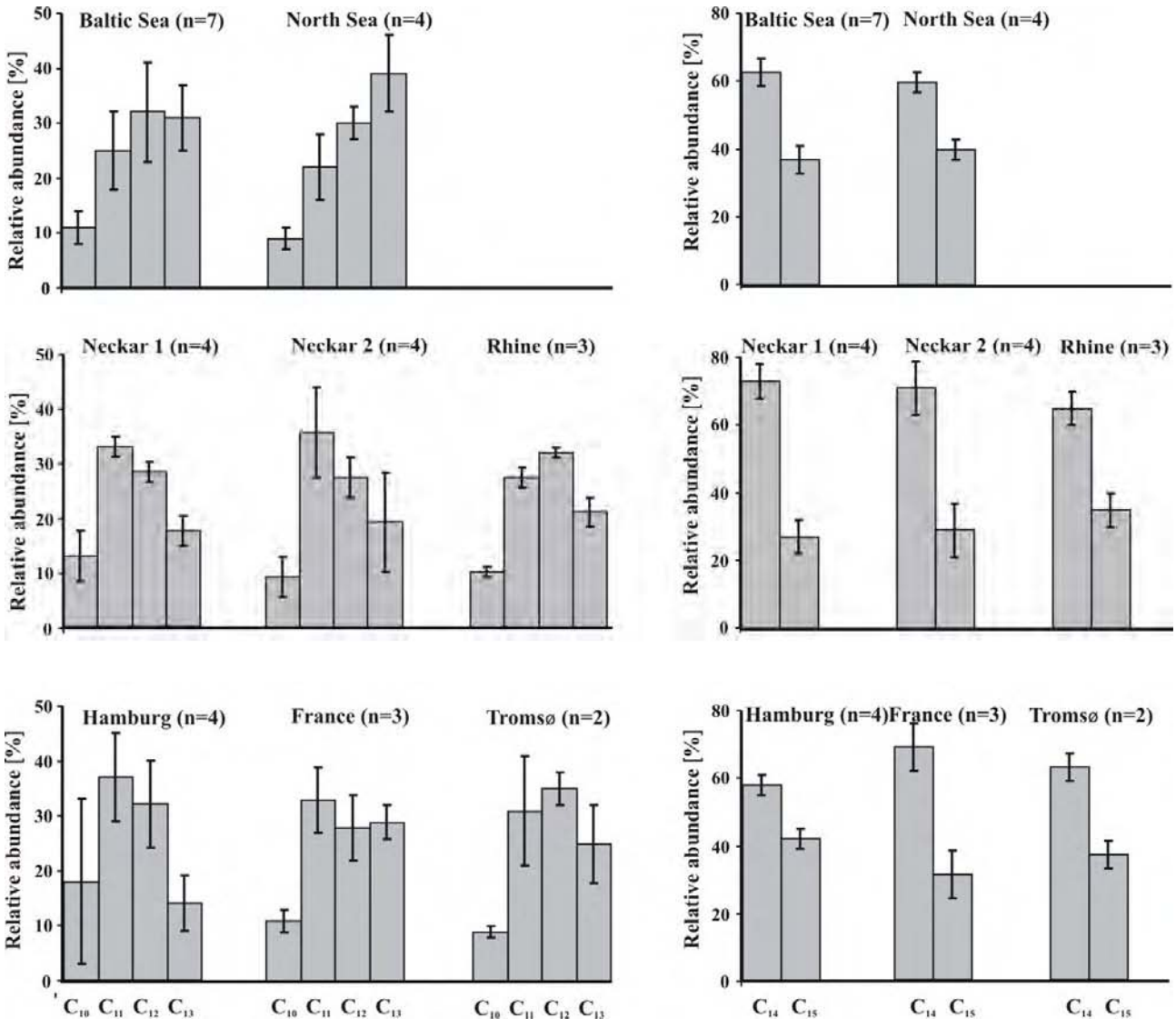

Figure 19. Relative distribution [%] of SCCP (left) and MCCP (right) compounds depending on the carbon chain length in sediments from the North and Baltic Sea, Seine estuary, harbours of Hamburg and Trømsø and suspended particular matter from Rhine and Neckar obtained by HRGC-ECNI-LRMS. Error bars of the average of samples from the same sampling site are given.

The calculated mean chlorine content was 59-64% for SCCP and 53-57% for MCCP in sediments and SPMs (see Tables 29 and 30). In general, suspended particular matter had higher mean chlorine content. Calculated molar masses in samples varied between 381-447 g/mol for SCCP and 425-460 g/mol for MCCP. Differences in SCCP patterns were obvious, whereas the MCCP patterns were quite similar in marine and freshwater sediments as well as in suspended particular matter (see Figure 19). Also, the homologue and congener group patterns for the same sampling sites (North Sea, Baltic Sea, Rhine, Neckar 1 and 2, Hamburg or Tromsø harbour) were in good agreement (see Tables 29 and 30 or Figure 19).

Table 29. Relative abundance [%] of SCCP and MCCP congeners, calculated average molecular masses [g/mol] and chlorine content [%] and main SCCP and MCCP components in sediments from the North and Baltic Sea (2003-2004). HRGC-ECNI-LRMS was employed.

	Molecular mass [g/mol]		**Chlorine content [%]**		**Relative abundance [%]**						**Main component**	
	SCCP	**MCCP**	**SCCP**	**MCCP**	**C_{10}**	**C_{11}**	**C_{12}**	**C_{13}**	**C_{14}**	**C_{15}**	**SCCP**	**MCCP**
North Sea												
KS 8 (2003)	417	452	60	56	9	19	22	50	62	38	$C_{13}Cl_6$	$C_{14}Cl_{7/8}$
KS 8 (2004)	404	453	60	56	11	30	30	29	59	40	$C_{11}Cl_7$	$C_{14}Cl_{7/8}$
KS 11 (2003)	424	455	61	57	8	18	34	40	63	37	$C_{13}Cl_7$	$C_{14}Cl_{7/8}$
KS 11 (2004)	418	455	61	56	7	23	32	39	55	44	$C_{13}Cl_7$	$C_{14}Cl_{6/7}$
Baltic Sea												
710 (2004)	395	452	59	56	12	34	22	32	61	40	$C_{13}Cl_6$	$C_{14}Cl_{6/7}$
715 (2004)	410	454	61	57	13	32	29	25	58	41	$C_{12}Cl_7$	$C_{14}Cl_{6/7}$
718 (2004)	403	451	60	56	14	30	25	31	68	31	$C_{13}Cl_6$	$C_{14}Cl_{6/7}$
721 (2004)	414	452	60	57	12	22	25	42	67	33	$C_{13}Cl_7$	$C_{14}Cl_{7/8}$
ODER	407	453	60	56	16	23	24	37	55	45	$C_{13}Cl_7$	$C_{14}Cl_{6/7}$
RUDEN	419	459	61	57	6	19	41	34	64	36	$C_{13}Cl_7$	$C_{14}Cl_{7/8}$
ECKFBU	415	455	61	57	8	22	48	22	64	35	$C_{12}Cl_{5/6}$	$C_{14}Cl_{7/8}$

Higher contents of C_{12} and C_{13} compounds were reported for urbanised areas (Kemmlein *et al.* 2002). C_{12} and C_{13} compounds were also most dominant in surface sediments from Lake Ontario harbors (42-81% of the relative abundance, 8 samples) (European Chemicals Bureau 2000). Štejnarová *et al.* (2005) also reported abundant chlorinated undecanes in sediments from three

different areas in the Czech Republic. Sediment samples influenced by local sources showed abundances between 40-81% for C_{12} and C_{13} compounds (European Commission 1999, Kemmlein *et al.* 2002, Stejnarova *et al.* 2005, UNECE ad hoc Expert Group on POPs 2003).

The less chlorinated, lower chain length congeners are reported to be more volatile components of commercial SCCP mixtures and are predominant in areas influences primarily by long range transport. Mainly C_{11} compounds were dominant in river sediments from a background area in the Czech Republic (Stejnarova *et al.* 2005).

Three of four sediment samples from Australia showed higher relative abundances for C_{15} (37-41%) compounds than C_{14} (Kemmlein *et al.* 2002). C_{16-17} congeners were also detected. One sediment sample from Canada (Detroit River) showed a MCCP pattern known for technical mixtures (Tomy and Stern 1999). The Czech sediment samples were dominated by C_{15} and C_{16} chains (around 80%). Mud from Rotterdam harbour was dominated by C_{14} congeners, two mud samples from Hamburg harbour by C_{15} and one mud flat from Holland by C_{14} chains (Greenpeace 1995). C_{17} compounds were detected in all samples. C_{14} congeners were the main CP compounds in sludge samples from urban/industrialized areas in England (Stevens *et al.* 2003).

Table 30. Relative abundance [%] of SCCP and MCCP congeners, calculated average molecular mass [g/mol] and chlorine content [%] and main SCCP and MCCP components in sediments and SPM samples from Europe. HRGC-ECNI-LRMS was employed.

	Molecular mass [g/mol]		Chlorine content [% Cl]		Relative abundance [%]						Main component	
	SCCP	MCCP	SCCP	MCCP	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	SCCP	MCCP
Seine 1	414	451	61	56	9	36	31	25	74	26	$C_{11}Cl_7$	$C_{14}Cl_7$
Seine 2	381	445	58	56	12	36	21	30	61	39	$C_{11}Cl_7$	$C_{14}Cl_7$
Seine 3	419	448	61	56	12	26	31	30	71	29	$C_{11}Cl_7$	$C_{14}Cl_7$
Hamburg												
Hamburg 1	447	442	65	55	9	45	31	16	59	41	$C_{11}Cl_8$	$C_{14}Cl_7$
Hamburg 2	440	435	64	55	5	32	43	20	61	39	$C_{12}Cl_8$	$C_{14}Cl_6$
Hamburg 3	414	441	64	55	39	28	23	10	59	41	$C_{10}Cl_7$	$C_{14}Cl_7$
Elbe	421	437	63	55	19	42	29	10	54	46	$C_{11}Cl_7$	$C_{15}Cl_6$
Tromsø												
Tromsø 1	424	446	63	53	9	38	33	20	66	34	$C_{11}Cl_7$	$C_{14}Cl_7$
Tromsø 2	429	453	62	57	10	24	37	30	60	40	$C_{12}Cl_8$	$C_{14}Cl_7$
Neckar 1												
August	426	465	63	58	12	36	32	21	69	31	$C_{11}Cl_7$	$C_{14}Cl_8$
September	423	460	63	57	12	39	32	17	67	33	$C_{11}Cl_7$	$C_{14}Cl_8$
November	424	458	63	57	21	35	28	16	79	21	$C_{11}Cl_7$	$C_{14}Cl_{7/8}$
December	433	465	63	58	10	34	32	23	74	26	$C_{12}Cl_8$	$C_{14}Cl_{7/8}$
Neckar 2												
August	438	457	63	57	6	30	32	33	62	38	$C_{12}Cl_8$	$C_{14}Cl_7$
September	428	457	63	57	8	35	33	24	67	33	$C_{11}Cl_7$	$C_{14}Cl_7$
November	427	442	63	56	13	43	31	14	78	22	$C_{11}Cl_8$	$C_{14}Cl_7$
December	431	455	64	57	14	50	24	12	78	22	$C_{11}Cl_8$	$C_{14}Cl_7$
Rhine												
August	429	455	63	57	11	30	36	24	65	35	$C_{12}Cl_7$	$C_{14}Cl_7$
September	421	460	62	57	10	29	34	27	60	40	$C_{12}Cl_7$	$C_{14}Cl_7$
December	429	452	63	57	12	33	36	20	71	29	$C_{12}Cl_8$	$C_{14}Cl_7$

The congener and homologue patterns of SCCPs and MCCPs ($C_{10\text{-}13}Cl_{5\text{-}10}$ and $C_{14\text{-}15}Cl_{5\text{-}10}$) observed in sediments were compared to those of technical mixtures from European producers (Table 29, 30 and 21). Results of the principal component analysis are shown in the score plot in Figure 20. The two principal components with the largest variance were selected.

The variances of PC 1 and PC 2 for SCCPs were 60.8 and 18.3%, respectively, and for MCCPs 77.5 and 10.4%. SCCP 55.5% Cl, Hordalub 80, Cereclor^{TM} 60L and the samples from the Seine (1 and 3), Rhine (September) and the North and Baltic Sea formed group I (see Figure 20 and Table 31, SCCP) with chlorine contents of 59-61%. Group II consisted of SCCP 63% Cl, Hordalub 500 and samples from Rhine, Neckar 1 and 2, Tromsø, Elbe and Hamburg 2 (see Table 31). These samples had a higher chlorination degree (around 63%) than the members of group I.

Hordalub 17, SCCP 51.5% Cl and sample Seine 2 had the lowest chlorine contents (around 58%) as well as molecular masses (< 385 g/mol). Cereclor^{TM} 70L, Hamburg 1 and Neckar 2 (December) represented the highest chlorine contents of 64-65%. Sample ECKFBU and Hamburg 3 were separated because of their different SCCP main components ($C_{12}Cl_{5/6}$ and $C_{10}Cl_7$). However, a good separation of marine samples from freshwater sediments and suspended particular matter samples was observed for SCCPs.

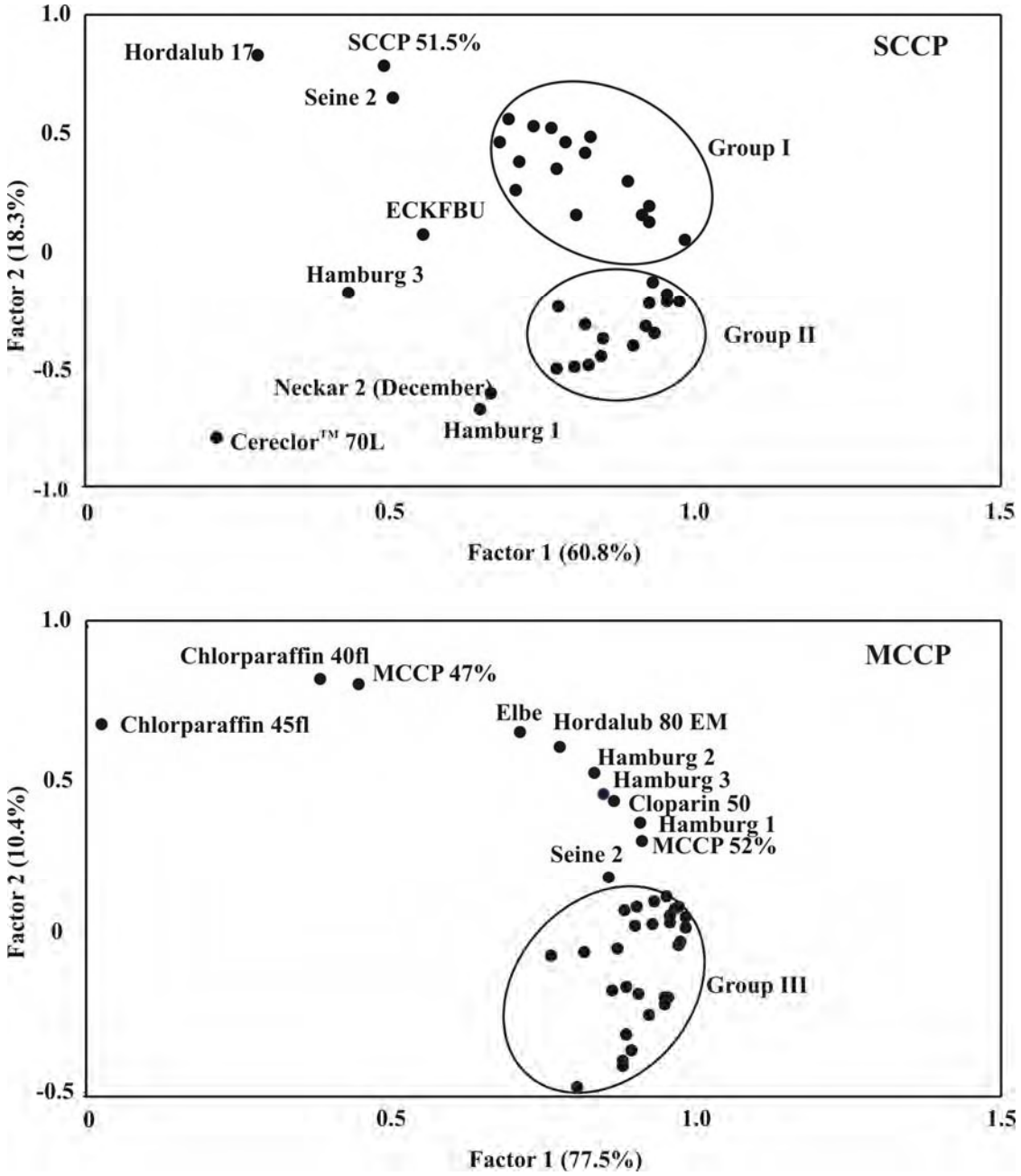

Figure 20. Principal component analysis of the SCCP and MCCP congener and homologue group patterns in marine and freshwater sediments, suspended particular matters and in technical mixtures from European producers. Data were obtained by ECNI-MS (see Table 24, 32 and 33). Three groups are marked in the scoreplots.

The separation in the score plot of the MCCPs is more difficult to explain due to the very similar patterns (see also Figure 20). Chlorparaffin 45fl had a higher relative abundance of C_{15} than C_{14}. The mixtures Chlorparaffin 40fl and MCCP 47% Cl had the lowest calculated chlorine contents of around 52%. Members of group III had a degree of chlorination ≥ 56%. Samples Elbe, Hamburg 1-

3, Seine 2, the technical mixtures Hordalub 80 EM, Cloparin 50 and MCCP 52% Cl showed a degree of chlorination < 56% (see Table 31).

Table 31. Members of group I, II and III of the principal component analysis of the SCCP and MCCP congener and homologue group patterns in marine and freshwater sediments, suspended particular matters and in technical mixtures from European producers. Data were obtained by ECNI-MS (see Table 24, 32 and 33).

Group	Marine Sediments	Freshwater sediments and SPM	CP Standard
I (SCCP)	715 (2004)	Seine 1 and 3	Cereclor^{TM} 60L
	718 (2004)	Rhine (September)	Hordalub 80
	721 (2004)		SCCP 55.5% Cl
	710 (2004)		
	ODER		
	RUDEN		
	KS 11 (2003, 2004)		
	KS 8 (2003, 2004)		
II (SCCP)		Rhine (August and December)	Hordalub 500
		Neckar 1 (August, September, November, December)	SCCP 63% Cl
		Tromsø 1 and 2	
		Hamburg 2	
		Elbe	
		Neckar 2 (August, September, November)	
III (MCCP)	715 (2004)	Seine 1 and 3	MCCP 57% Cl
	718 (2004)	Tromsø 1 and 2	Hordaflex SP
	721 (2004)	Neckar 1 (August, September, November, December)	Cereclor^{TM} S52
	710 (2004)		
	ODER	Neckar 2 (August, September, November, December)	
	RUDEN		
	ECKFBU	Rhine (August, September and December)	
	KS 11 (2003, 2004)		
	KS 8 (2003, 2004)		

PCA analysis clearly differentiated the SCCP patterns obtained from the North and Baltic Sea sediments and from the river sediments and suspended particular matter. This observation could be the result of shift in industrial usage or manufacturing patterns in favour of heavier chlorinated SCCP technical mixtures. However, both groups showed similarities with technical mixtures with

different chlorine content. This similarity indicated industrial origin and a diffuse input of chloroparaffins (additives in paints etc.) in the environment. Surprisingly, the observed SCCP and MCCP patterns in sediments were similar to technical mixtures from Hoechst, which stopped production in 1998. Another explanation could be, that the differences in CP pattern between actual produced/used technical mixtures and former ones are marginal (producer ICI and Caffaro). No changes in CP pattern in sediments as well as suspended particular matter compared to technical mixtures excluded degradation or transformation of CPs in the environment.

4.4.3 Quantification by CACI-LRMS

CP levels in marine sediments were also determined by CACI-MS. Samples from different years were available for six sampling sites (see Figure 21). SCCP and MCCP (C_{14-15}) levels were in the range of 13-128 ng/g and 42-303 ng/g d.w.

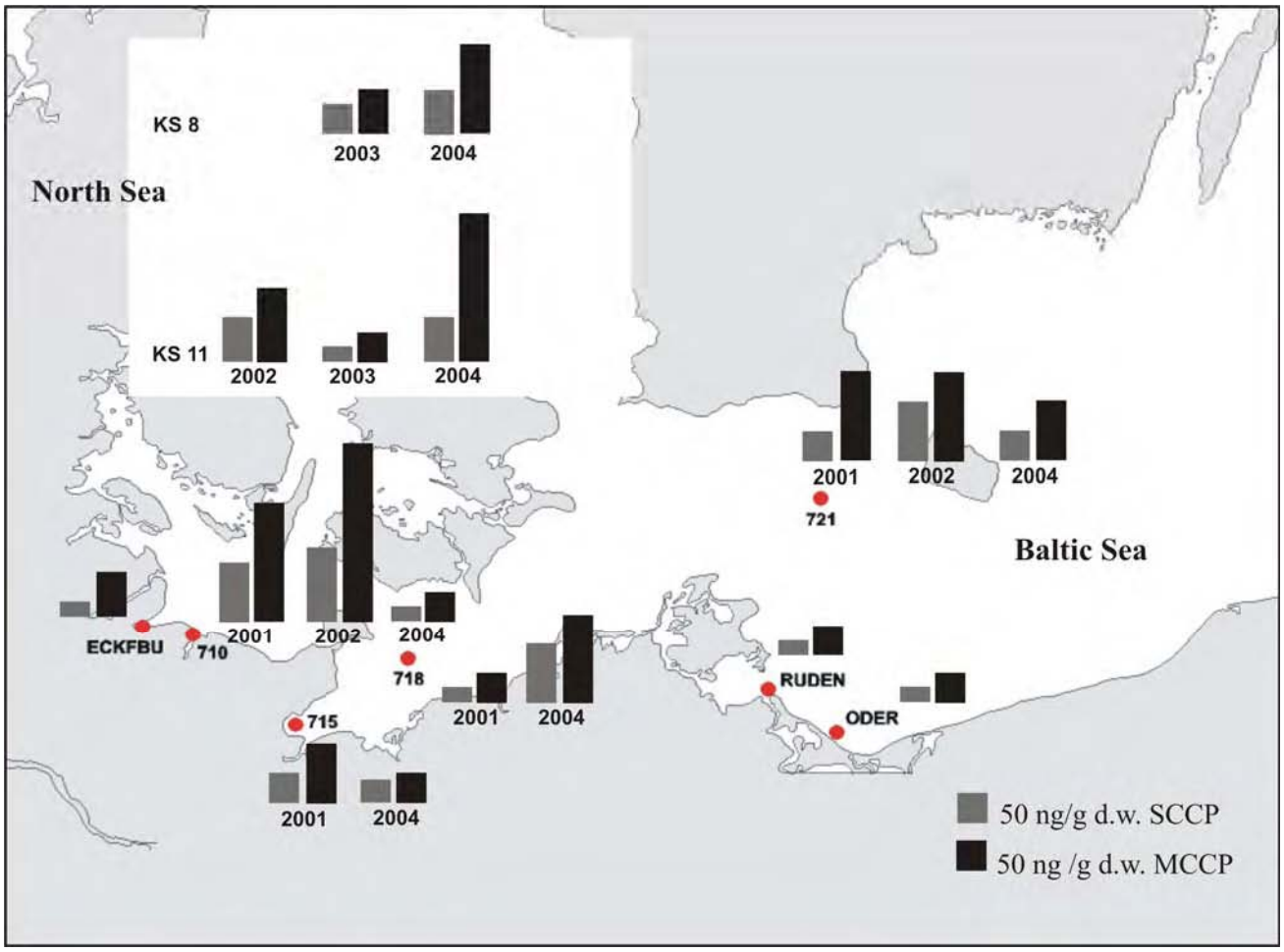

Figure 21. Sampling sites (2001-2004) in the North and Baltic Sea as well as SCCP and MCCP concentrations [ng/g dry weight] obtained by HRGC-CACI-LRMS.

Ionization by CH_4/CH_2Cl_2 formed exclusively chlorine adducts and eliminated mass interferences by $[M]^-$ and $[M\text{-}Cl]^-$ typical for ECNI (see chapter Introduction). Therefore, minor C_{16} congener levels were quantified in the presence of chlorinated undecanes by CACI-MS (Table 32). Concentrations were at maximum 12% higher than the results including only chlorinated C_{14} and C_{15} congeners. In general, the concentrations obtained by CACI-MS were higher as for ECNI-MS (4-125% for SCCP, 0-202% for MCCP and 12-127% for S+MCCP, eleven samples). The ratios of MCCP/SCCP varied between 1.5 and 3.2 and were similar (< 25%) for different years (see Table 32).

Table 32. SCCP and MCCP concentrations [ng/g dry weight] determined in sediments from the North and Baltic Sea by HRGC-CACI-LRMS. Ratios of MCCP/SCCP are also given.

Sample	SCCP ΣC_{10-13}	MCCP ΣC_{14-15}	MCCP ΣC_{14-16}	S+MCCP ΣC_{10-15}	MCCP/SCCP
	[ng/g dry weight]				
Baltic Sea					
710 (2001) [a]	98	199	n.d.	297	2.0
710 (2002) [a]	128	303	n.d.	431	2.4
710 (2004) [b]	13	36	37	49	2.8
715 (2001) [a]	48	91	n.d.	139	1.9
715 (2004) [b]	35	51	54	86	1.5
718 (2001) [a]	21	48	n.d.	69	2.3
718 (2004) [b]	82	141	149	223	1.7
721 (2001) [a]	105	131	n.d.	236	1.2
721 (2002) [a]	91	153	n.d.	244	1.7
721 (2004) [b]	44	74	81	118	1.7
ECKFBU [b]	29	70	77	99	2.4
ODER [b]	18	42	43	60	2.4
RUDEN [b]	25	58	61	83	2.3
North Sea					
KS 8 (2003) [b]	30	70	76	100	2.3
KS 8 (2004) [b]	62	145	149	207	2.3
KS 11 (2002) [a]	72	132	n.d.	204	1.8
KS 11 (2003) [b]	18	54	58	72	3.0
KS 11 (2004) [b]	79	250	275	329	3.2

[a] quantification with SCCP and MCCP standard (55.5 and 57.0% Cl); n.d. not determined; [b] average of quantification with three SCCP (51.5, 55.5 and 63% Cl) and three MCCP standards (47, 52 and 57% Cl) according Tomy *et al.* (1997)

Results of CACI-MS were in better agreement than ECNI with the results obtained by EI-MS/MS (2-29% deviation) for eleven sediment samples. It seemed that the ionization of CPs was disturbed in the ECNI mode than with CACI (see Figure 22). Other chlorinated compounds like PCBs and HCHs can not be removed by the sample clean-up as shown in chapter 4.1.2. Coelution of such compounds with the broad CP signals interferes with the quantification by low resolution MS. CACI-MS suppressed the ionization of these compounds and enhanced selectivity for CP. The application of high resolution MS is another possibility to exclude such interferences.

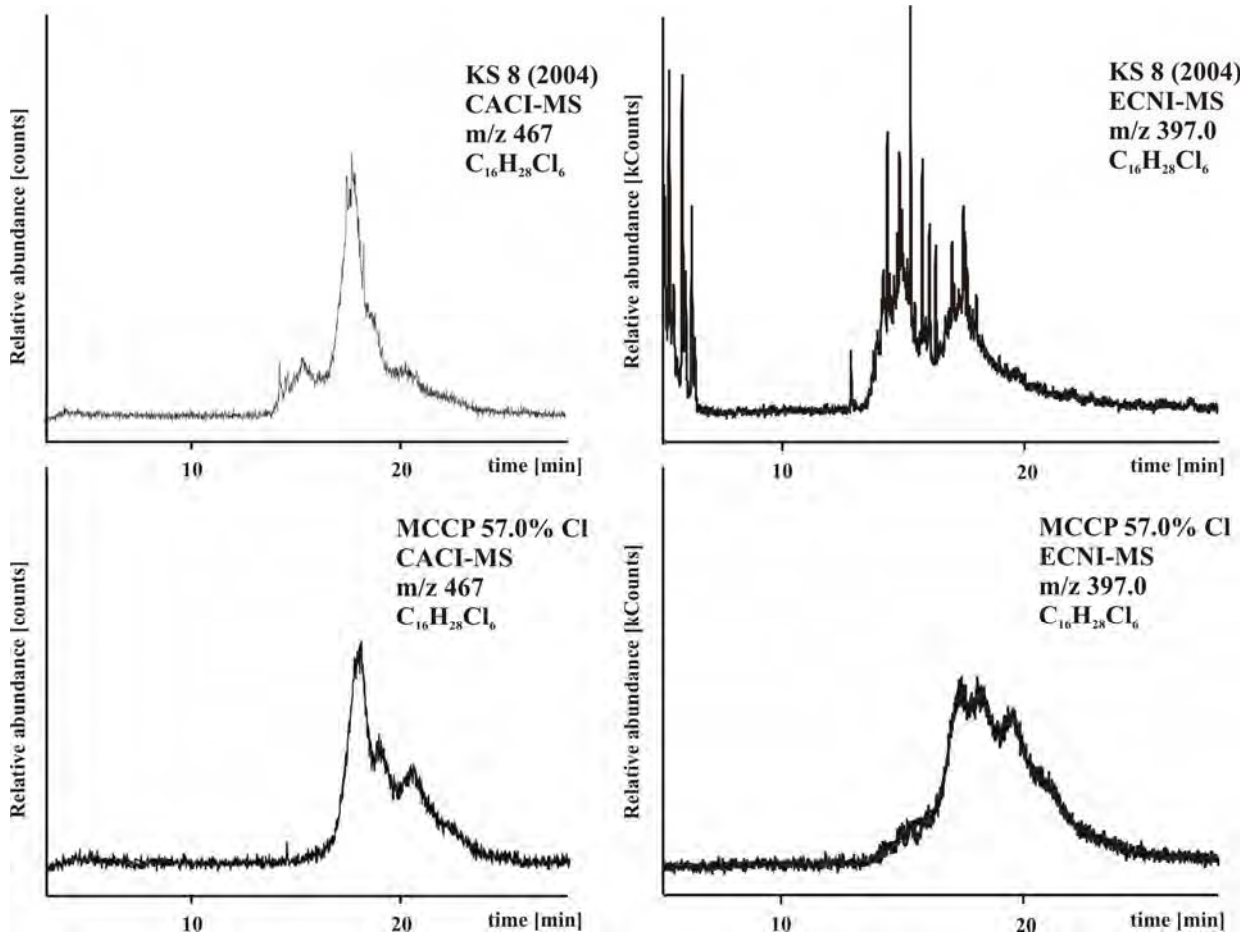

Figure 22. Disturbance of quantification of the congener group $C_{16}H_{28}Cl_6$ by ECNI-MS in sample KS 8 (2004) by CP congener overlap and its suppression by CACI-MS. The MCCP standard with 57.0% Cl is shown for assignment of retention time range and comparison of peak shape.

4.4.3.1 Comparison of CP congener and homologue patterns in marine sediments and technical CP mixtures

Eighteen sediment samples from the North and Baltic Sea were also investigated by CACI-MS. Table 33 shows the results. Tri- and tetradecanes with 4-5 chlorine atoms were the predominant compounds in the samples (except 710, 718 and 721 from 2001). The distribution of the homologues was comparable to ECNI-MS for the same samples (see Table 29). The calculated chlorine content was 53-56% for SCCP and 45-50% for MCCP in sediments. CP patterns obtained

for different years were in good agreement for the same sampling site. Only sample 721 from 2001 showed a completely different SCCP pattern compared to 2002 and 2004.

Table 33. Relative abundance [%] of the SCCP ($C_{10-13}Cl_{4-10}$) and MCCP ($C_{14-15}Cl_{4-10}$) congeners, calculated average molecular masses [g/mol] and chlorine content [%] and main SCCP and MCCP components in sediments from the North and Baltic Sea. HRGC-CACI-LRMS was employed.

	Molecular mass [g/mol]		Chlorine content % Cl		Distribution [%]						Main component	
	SCCP	MCCP	SCCP	MCCP	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	SCCP	MCCP
Baltic Sea												
710 (2001)	379	394	55	49	6	10	45	40	65	35	$C_{12}Cl_6$	$C_{14}Cl_5$
710 (2002)	358	373	54	47	8	25	28	38	78	22	$C_{13}Cl_4$	$C_{14}Cl_4$
710 (2004)	337	390	54	49	15	20	25	39	70	30	$C_{13}Cl_4$	$C_{14}Cl_4$
715 (2001)	361	387	53	48	8	11	39	42	59	41	$C_{13}Cl_4$	$C_{14}Cl_5$
715 (2004)	341	382	53	48	13	20	28	39	67	33	$C_{13}Cl_4$	$C_{14}Cl_4$
718 (2001)	358	381	56	48	33	16	23	27	70	30	$C_{10}Cl_8$	$C_{14}Cl_4$
718 (2004)	338	374	53	47	13	21	29	38	67	33	$C_{13}Cl_4$	$C_{14}Cl_4$
721 (2001)	391	391	55	49	6	7	9	78	62	38	$C_{13}Cl_7$	$C_{14}Cl_6$
721 (2002)	364	378	54	47	7	35	27	31	70	30	$C_{13}Cl_4$	$C_{14}Cl_4$
721 (2004)	344	394	53	49	13	19	27	42	64	36	$C_{13}Cl_4$	$C_{14}Cl_4$
ECKFBU	350	391	53	49	0	23	32	45	63	37	$C_{13}Cl_4$	$C_{14}Cl_4$
ODER	337	371	53	46	15	22	28	36	70	30	$C_{13}Cl_4$	$C_{14}Cl_4$
RUDEN	342	379	53	47	12	21	28	38	64	36	$C_{13}Cl_4$	$C_{14}Cl_4$
North Sea												
KS 8 (2003)	345	397	53	50	8	17	28	47	64	36	$C_{13}Cl_4$	$C_{14}Cl_4$
KS 8 (2004)	334	364	53	45	16	23	28	33	70	30	$C_{13}Cl_4$	$C_{14}Cl_4$
KS 11 (2002)	348	365	53	46	10	25	30	34	81	19	$C_{13}Cl_4$	$C_{14}Cl_4$
KS 11 (2003)	341	371	53	46	14	22	25	40	71	29	$C_{13}Cl_4$	$C_{14}Cl_4$
KS 11 (2004)	358	388	53	49	0	20	32	48	68	32	$C_{13}Cl_5$	$C_{14}Cl_4$

The SCCP ($C_{10-13}Cl_{4-10}$) and MCCP ($C_{14-15}Cl_{4-10}$) patterns of sediments were compared to these of technical mixtures. Results of the principal component analysis are shown in the score plot in Figure 23. The two principal components with the largest variance were selected and were in total 80.1% for SCCP and 91.1% for MCCP. Cereclor™ 70L had as the only one a chlorination degree of > 65% and was separated from the rest. Also, SCCP 63% Cl, Hordalub 500 and Cereclor™ 60L had higher chlorine contents as the samples. The sample 710 (2001) had the same SCCP main

components as SCCP 55.5% and Hordalub 80 ($C_{12}Cl_6$ respective $C_{12}Cl_{5/6}$). Due to the completely different CP pattern (78% of C_{13} chains) sample 721 (2001) was separated from all other sediment samples. The majority of the marine samples had comparable patterns to the lower chlorinated mixtures SCCP 51.5% and Hordalub 17.

In the score plot of the MCCPs (see Figure 23), Chlorparaffin 45fl was separated from the rest due to the completely different pattern (abundance of C_{15} congeners > C_{14}). The mixtures MCCP 57% Cl and Hordaflex SP had the highest observed chlorine contents of all investigated mixtures and samples (> 52% Cl). Cereclor^{TM} S52 and MCCP 52% Cl had a chlorine content of around 51 %. Main components were $C_{14/15}Cl_{5/6}$. The CP patterns of sample 710 and 721 from 2001 were similar to Hordalub 80 EM and Cloparin 50. The sample majority (group II) had chlorine contents of around 51%. Their congener and homologue group patterns were similar to that of MCCP 47% Cl.

SCCP patterns in marine sediments were similar to technical mixtures with lower chlorine content as observed for ECNI-MS. MCCP patterns were similar to the already phased out mixtures from Hoechst (Chlorparaffin 40fl and Hordalub 17). For time periods of 2-3 years no change in the CP pattern could be observed in sediments (see Table 33). This indicated no degradation or transformation of SCCPs and MCCPs under environmental conditions.

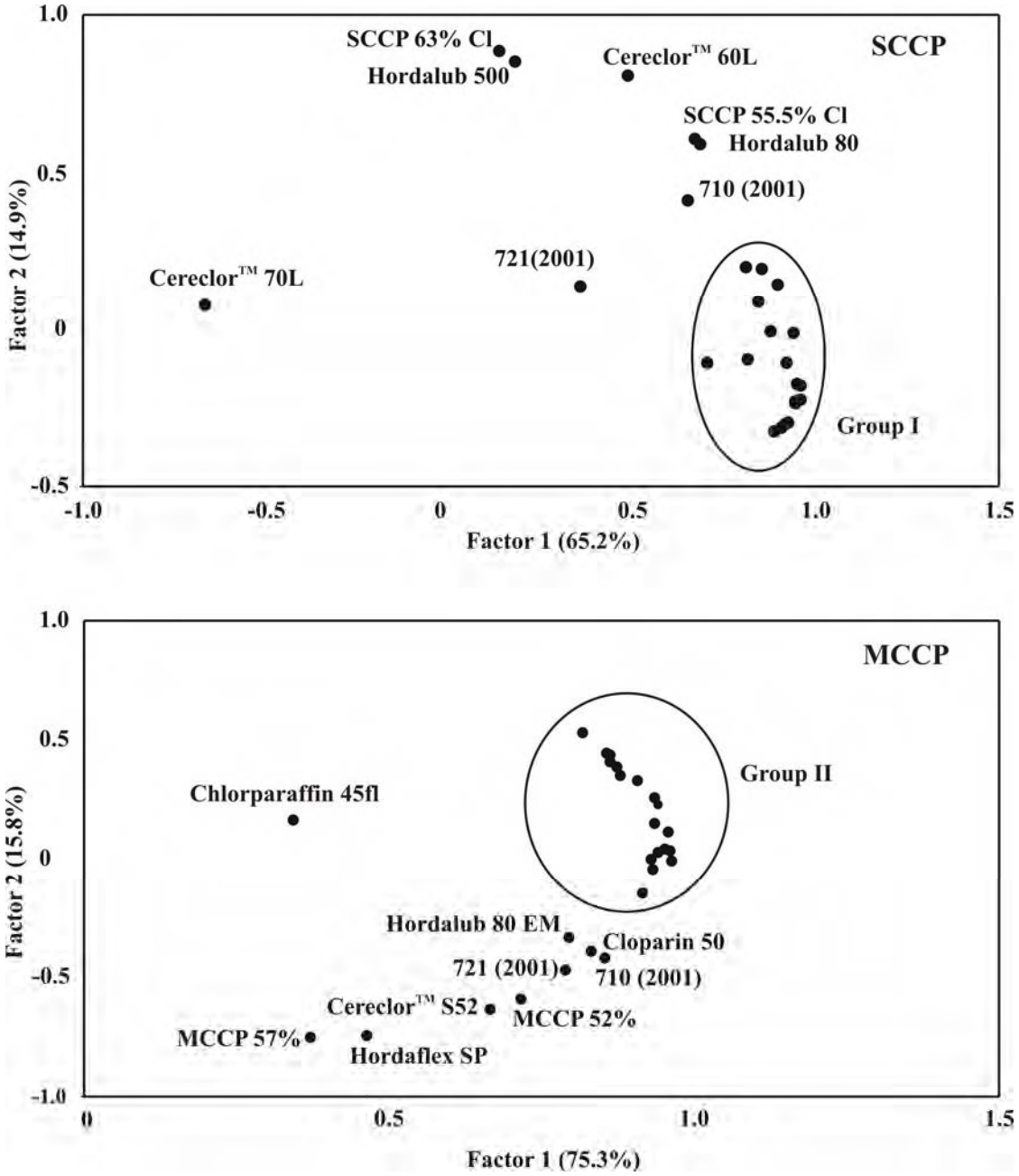

Figure 23. Principal component analysis of the SCCP and MCCP congener and homologue patterns in marine and freshwater sediments, suspended particular matters and in technical mixtures from European producers obtained by CACI-MS (see Table 35 and 25). Two groups are marked in the score plots.

Group I: SCCP 51.5% Cl, Hordalub 17, 710 (2002 and 2004), 715 (2001), 718 (2001 and 2004), 721 (2002, 2004), ODER, RUDEN, ECKFBU, KS 8 (2003, 2004), KS 11 (2002, 2003 and 2004)

Group II: MCCP 47% Cl, Chlorparaffin 40fl, Hordalub 17, 710(2002 and 2004), 715 (2001), 718 (2001 and 2004), 721 (2002, 2004), ODER, RUDEN, ECKFBU, KS 8 (2003, 2004), KS 11 (2002, 2003 and 2004)

4.4.4 Comparison of congener and homologue patterns in marine sediments obtained by ECNI-MS and CACI-MS

The chlorine content ratio of ECNI-MS and CACI-MS determination was higher for sediments from the North and Baltic Sea for 2003-2004 (1.16±0.03 for SCCP and 1.20±0.03 for MCCP, see Table 36) than for technical mixtures (see Table 34).

Table 34. Comparison of the calculated average molecular masses [g/mol] and average chlorine contents [% Cl] for SCCP and MCCP in sediments obtained by HRG-ECNI-LRMS and HRGC-CACI-LRMS.

Sample		% Cl		Molecular mass [g/mol]	
		SCCP	MCCP	SCCP	MCCP
KS 8 (2003)	ECNI-MS [a]	61	56	424	455
	CACI-MS [b]	53	50	341	400
KS 8 (2004)	ECNI-MS	60	56	404	458
	CACI -MS	53	45	334	366
KS 11 (2003)	ECNI-MS	61	56	424	460
	CACI -MS	53	47	341	381
KS 11 (2004)	ECNI-MS	61	56	418	461
	CACI -MS	53	48	358	392
710 (2004)	ECNI-MS	59	56	395	455
	CACI -MS	53	49	337	391
715 (2004)	ECNI-MS	61	56	410	457
	CACI -MS	53	48	341	384
718 (2004)	ECNI-MS	60	56	403	453
	CACI -MS	53	46	338	377
721 (2004)	ECNI-MS	61	56	419	454
	CACI -MS	53	49	342	398
ECKFBU (2004)	ECNI-MS	61	56	415	456
	CACI -MS	53	49	350	395
ODER (2004)	ECNI-MS	60	56	405	454
	CACI -MS	53	46	337	373
RUDEN (2004)	ECNI-MS	61	56	419	462
	CACI -MS	53	47	342	382

[a] Determination of $C_{10\text{-}16}Cl_{5\text{-}10}$ and [b] $C_{10\text{-}16}Cl_{4\text{-}10}$

Table 33 also lists the main SCCP and MCCP congeners present in sediments. $C_{13}H_{24}Cl_4$ was the main SCCP congener and $C_{14}H_{26}Cl_4$ the main MCCP congener in nearly all samples (eleven samples from 2003-2004) when CACI-MS was used for detection. A similar Cl-atom shift as for technical mixtures was observed between CACI- and ECNI-MS (see Figure 24). Both ionisation techniques gave comparable relative abundances for SCCP congeners with the same carbon chain length (see Table 29 and 33). Coeluting compounds, not removed by the clean-up procedure disturbed somewhat quantification by ECNI-MS (see example in Figure 25) but not by CACI-MS, which suppressed ionisation of these interferences.

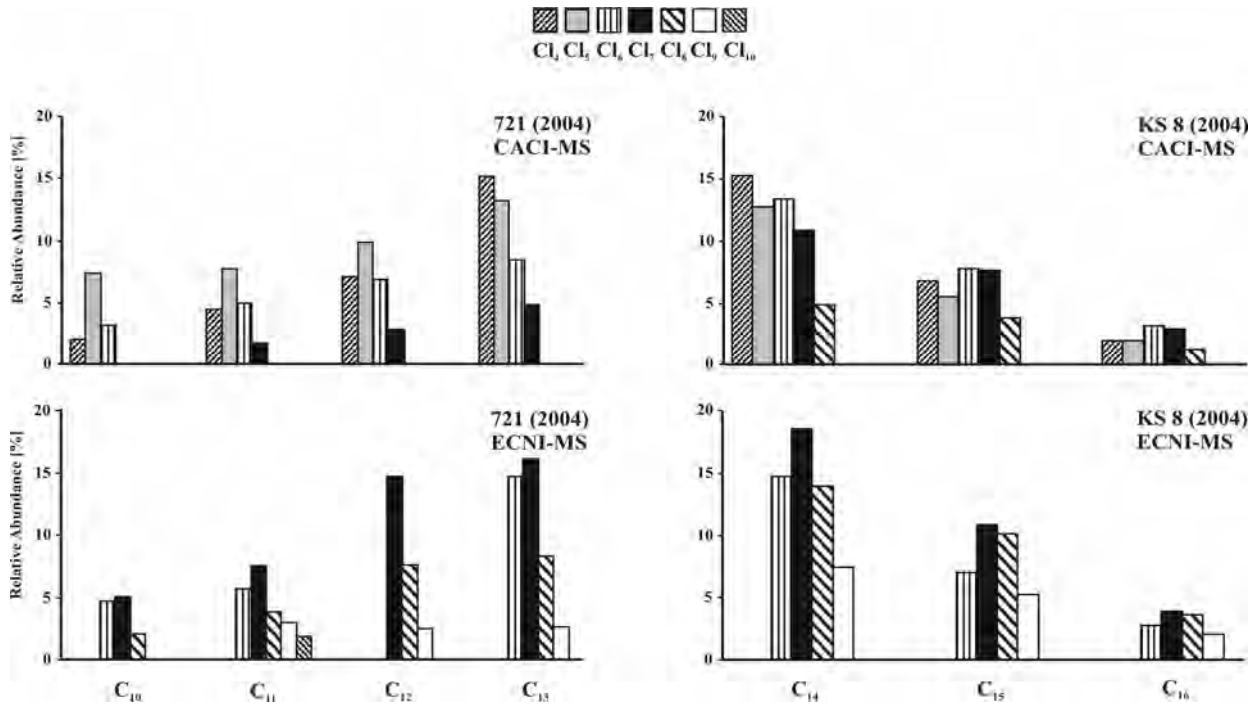

Figure 24. Congener and homologue patterns of two selected sediment samples obtained by HRGC-ECNI-LR MS and HRGC-CACI-LRMS.

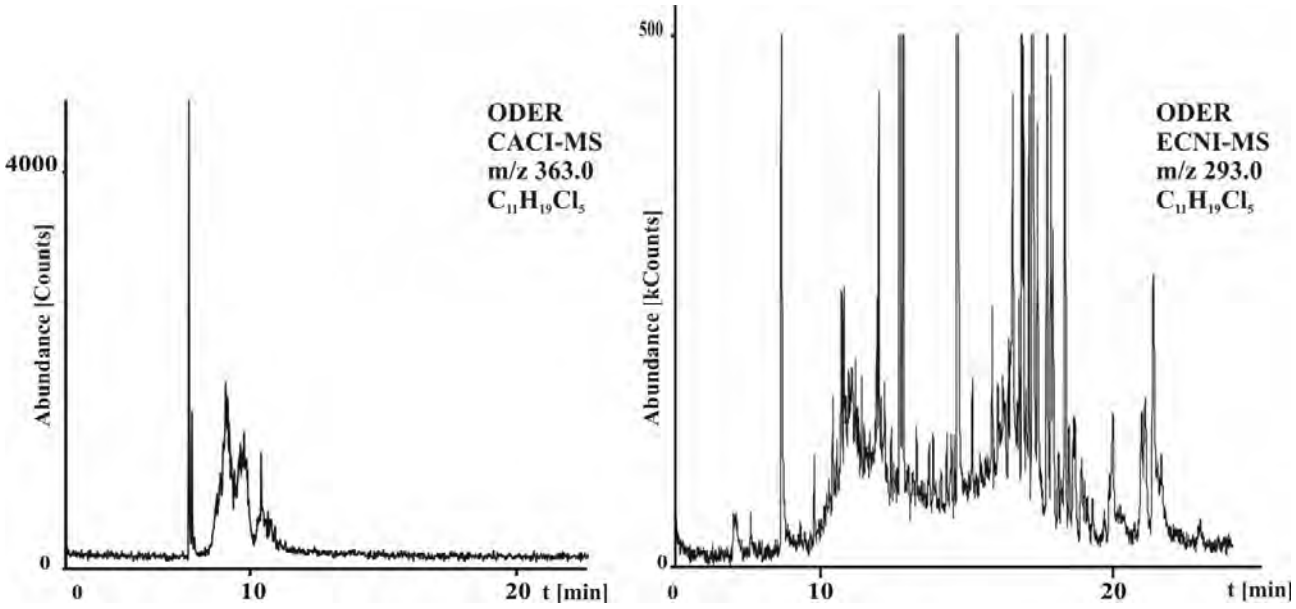

Figure 25. Interferences of ECNI-MS quantification of the congener group $C_{11}H_{19}Cl_5$ in sample ODER by interfering substances and suppression by CACI-MS.

4.4.5 Separation by GC×GC-LRMS

Sediment and suspended particular matter samples were analyzed by GC×GC-ECNI-MS in the scan mode. The chromatograms were overlaid with chromatograms of SCCPs (51.5, 55.5 and 63% Cl) and MCCPs (47, 52 and 57% Cl) (see Figure 26). The CP peak bands of SCCP are marked with a solid line and those of MCCPs with a dotted line. LCCP mixtures with 35, 42 and 50% Cl (concentration of 100 ng/µL) were also injected, but it was impossible to detect anything in the scan mode due its low volatility.

The GC×GC patterns of the samples showed differences. The chromatogram of the Tromsø 1 sediment showed intensive bands for CP compounds with C+Cl sum of 17, 18, 19, 20 and 21. ECNI-MS measurements showed that C_{11}, C_{12} and C_{13} compounds with 7 and 8 chlorine atoms had a relative abundance of 59% and C_{14} chains with 6 and 7 chlorine atoms of total 38%. The

calculated chlorine content was 63% for SCCP and 53% for MCCP. It was more or less the same for sample Hamburg 1. Calculated chlorine contents were in the same range than those for Tromsø 1 (see Table 30). Surprisingly, the chromatogram of KS 8 (2004) showed intensive bands for the C+Cl sum 15, 16 and 17. However, main components determined by one dimensional GC were C_{12} and C_{13} with 6 and 7 chlorine atoms (relative abundance in total of 44%) and C_{14} with 6 to 8 chlorine atoms (51%). Intensive bands should be expected for the C+Cl sum of 18, 19, 20, 21 and 22. No explanation could be given for this shift so far.

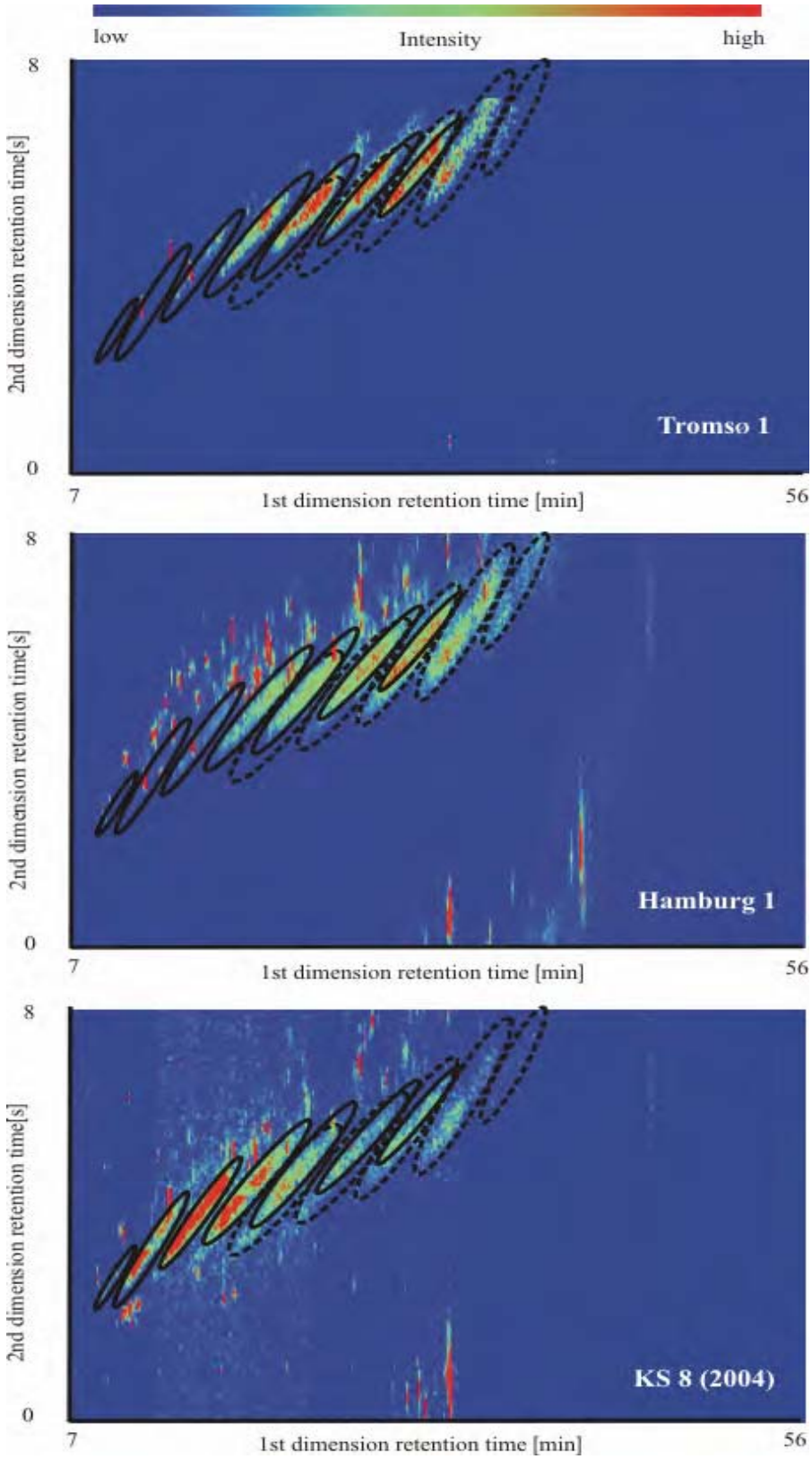

Figure 26. GC×GC-ECNI-MS extracted ion chromatograms ($[M\text{-}Cl]^-$ for $C_{10\text{-}15}Cl_{5\text{-}10}$) of selected samples. SCCP and MCCP peak areas are marked with a solid or dotted line.

4.5 Risk assessment of chloroparaffins

Short chain chlorinated paraffins have caused cancer in animal experiments. Therefore, SCCPs are considered as “non-threshold toxicants”, substances for which it is believed that there is a chance of adverse effects at any level of exposure (Government of Canada 1993). However, owing to the lack of information about exposure concentrations and estimations of levels to cause adverse effects, it is difficult to carry out risk assessment for animals.

The ratio between the predicted environmental concentrations (PEC) and the predicted no effect concentrations (PNEC) indicates a potential concern, if > 1 (European Commission 1999). PNEC values of around 0.8 or 20 µg/g dry weight or wet weight were estimated during laboratory studies with sediment-dwelling organisms or based on theoretical approaches (see Table 35). SCCP and MCCP concentrations in this study varied between 8-144 ng/g dry weight and between 22-407 ng/g (see Table 28). Therefore, SCCP and MCCP concentrations in sediments give PEC/PNEC ratios < 1. No significant risk is indicated to sediment dwelling organisms.

However, the calculated PEC/PNEC ratio has to be multiplied by an assessment factor of 10 for substances with a log K_{ow}> 5 according to the EU Technical Guidance Document (European Commission 1999). The factor takes into account the ingestion and bioaccumulation of substances by sediment-dwelling organisms. Then, SCCP and MCCP concentrations > 100 ng/g d.w. will lead to PEC/PNEC ratios > 1 for the PNEC values 0.88 µg/g (SCCP) and 1 µg/g (MCCP, see Table 35). For this case, further information and/or testing should be carried out to refine both PEC and PNEC values (e.g. monitoring data, toxicity studies on sediment-dwelling organisms).

Table 35. Summary of predicted no effect concentrations of chloroparaffins [µg/g].

	CP mixture	Effect concentration	Literature
Study			
Chironomus riparius, *Lumbriculus variegatus*	C_{14-17}, 52% Cl	$PNEC_{Sed}$: 1 µg/g w.w. (assessment factor of 50)	(European Chemicals Bureau 2002)
Theoretical approch			
Technical Guidance Document (EU TGD)	C_{10} and C_{13}, 55% Cl	$PNEC_{Sed}$: 21 µg/g d.w. (assessment factor of 10)	(UNECE ad hoc Expert Group on POPs 2003)
Canada	C_{10} and C_{13}, 55% Cl	$NOEC_{benthic}$: 20 µg/g d.w.	(Di Toro *et al.* 1991)
EU (based on TGD)	C_{10-13}, $\log K_{ow} > 5$	$PNEC_{Sediment}$: 0.88 µg/g (assessment factor of 10)	(European Commission 1999)

TGD: Technical Guidance Document; PNEC: Predicted No Effect Concentration; NOEC: No Observed Effect Concentration; w.w. wet weight; d.w.: dry weight

4.6 Chlordane levels in marine sediments

cis/trans-Chlordan and *cis/trans*-nonachlor were determined in marine samples from 2001-2004 (see Figure 27 and 28). The concentrations were in the range of < 2-139 pg/g d.w. for *trans*-chlordane, < 7-126 pg/g d.w. for *cis*-chlordane, < 2-29 pg/g d.w. for *cis*-nonachlor and 7-444 pg/g d.w. for *trans*-nonachlor (Table 36). Heptachlor was observed only in two samples from the Baltic Sea (ODER and RUDEN). Rapid transformation of heptachlor under environmental conditions is known. The concentrations of oxychlordane, *cis*- and *trans*-heptachlorepoxide were below the limits of detection in all sediments or were not detectable in sediments due to the instability of these compounds against acid during clean-up. Higher concentrations were observed in sediments from the Baltic Sea and for sampling sites KS 8 and KS 11 (North Sea) which are situated in the Elbe estuary. In general, the concentrations of *cis*- and *trans*-chlordane were always higher than *cis*-nonachlor in sediments from the North Sea. Highest concentrations of *trans*-chlordane were determined in the open sea (UE 70 and 67). In most cases *trans*-chlordane levels were similar or higher as *cis*-chlordane levels.

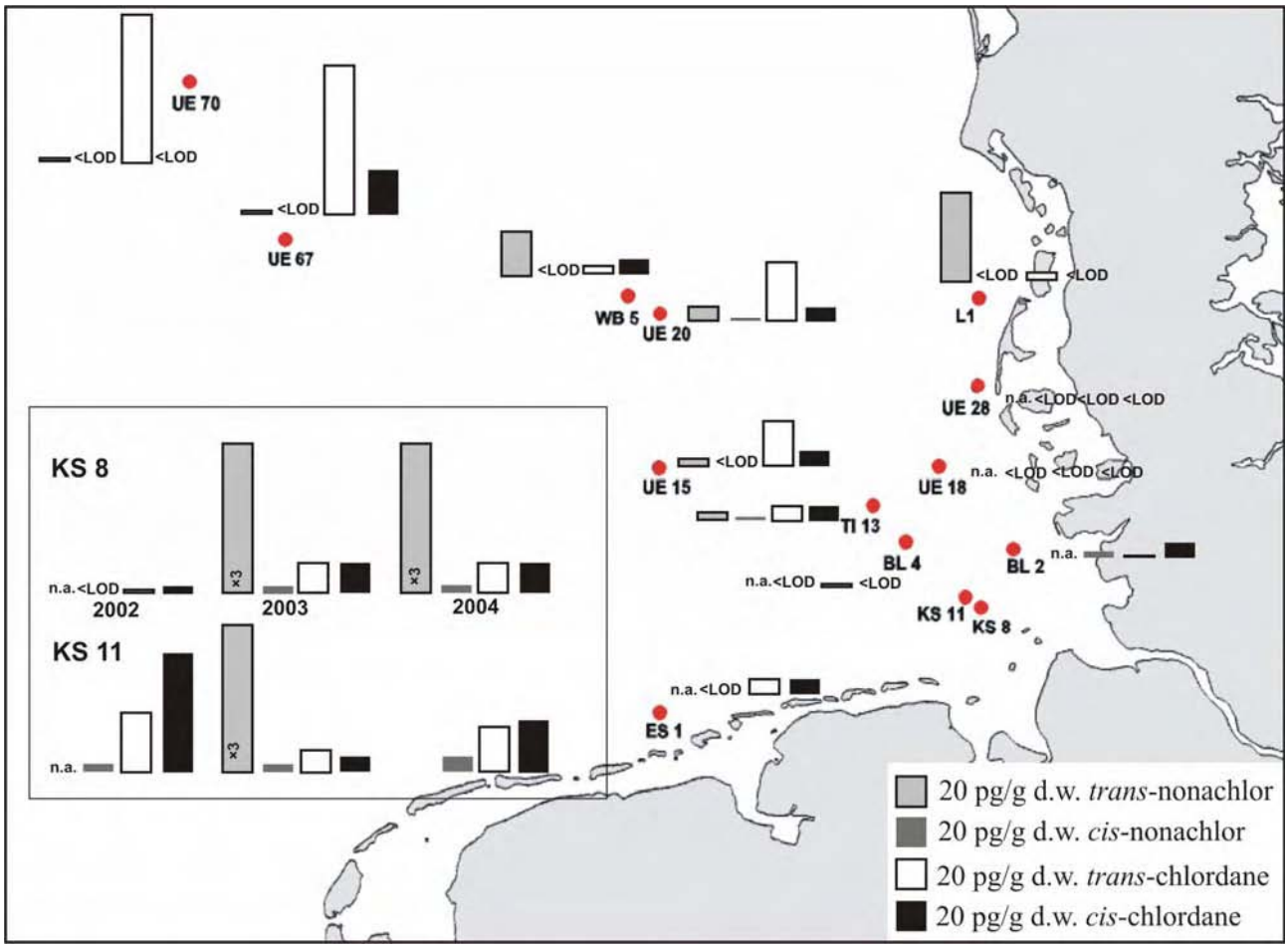

Figure 27. Concentrations of chlordane compounds [pg/g dry weight] in sediments from 2002, 2003 and 2004 in the North Sea. HRGC-ECNI-LRMS was employed (HP 5989II).

Location KS 11 was always highest contaminated sampling site in the North Sea as also observed for CPs. The concentrations in the Baltic Sea were higher than in the North Sea. Concentrations on TOC basis were more or less in the same range for the North and Baltic Sea (see Table 36). Levels and chlordane patterns for different years were in good agreement. The levels of *cis*- and *trans*-chlordane were always higher than for *cis*-nonachlor and levels of *trans*-chlordane were higher than for *cis*-chlordane in the Baltic Sea.

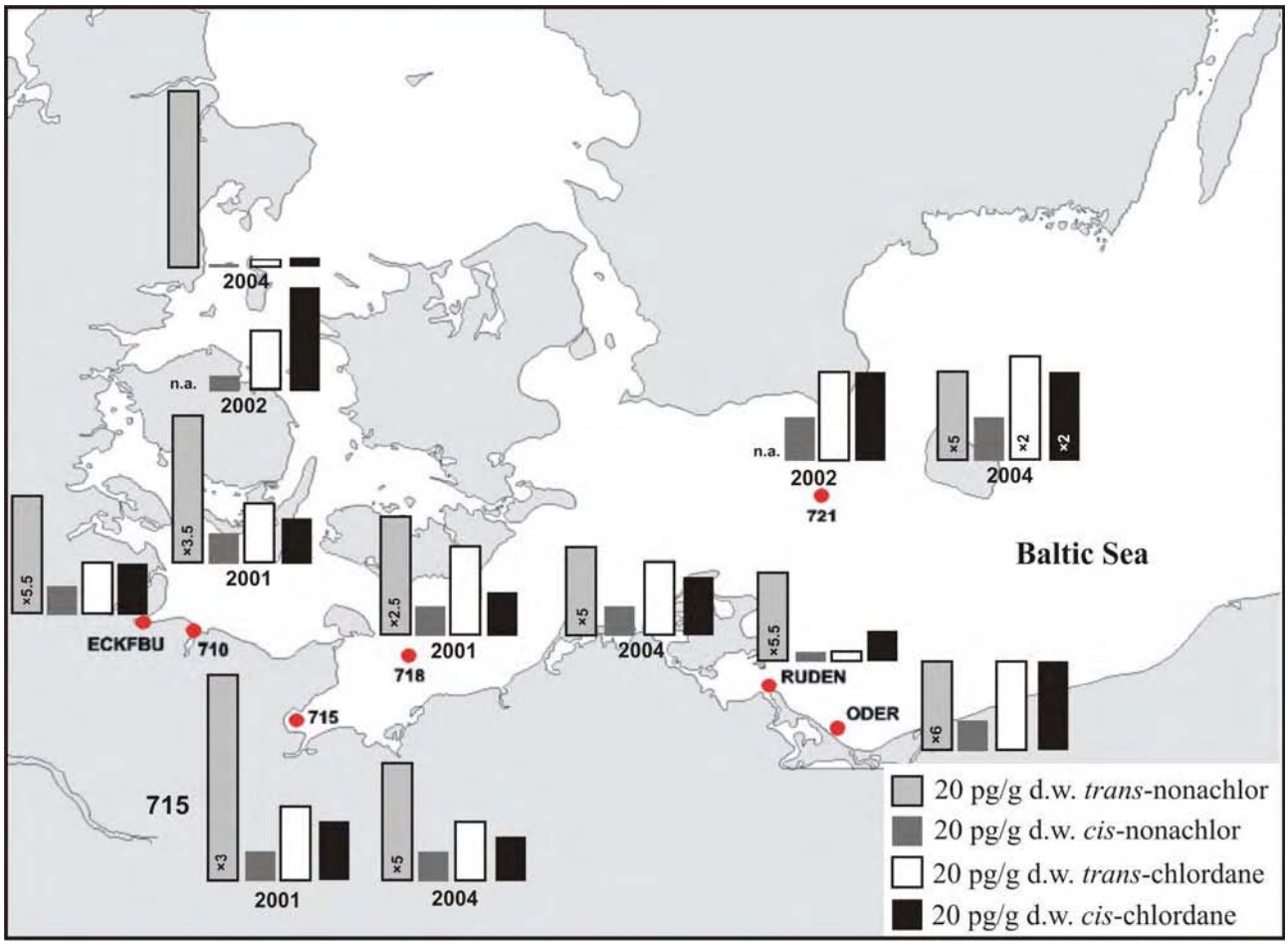

Figure 28. Concentrations of chlordane compounds [pg/g dry weight] in sediments from 2001, 2002, 2003 and 2004 in the Baltic Sea. HRGC-ECNI-LRMS was employed (HP 5989II).

The concentrations of *trans*-nonachlor were always highest in sediments. No explanation can be given for this phenomenon so far. Quantification with a new standard solution made from crystallized *trans*-nonachlor gave the same results. Also the measurements on two different instruments (Varian 1200L and HP 5989B) with two different ionization techniques (ECNI-MS and EI-MS/MS) led to the same results (see Tables 19 and 20). Matrix effects were excluded by standard addition. Reintegration of the chromatograms by a second person led to the same results.

Table 36. Chlordane concentrations [pg/g dry weight and ng/g TOC] in sediments collected 2001, 2002, 2003 and 2004. Data were obtained by HRGC-ECNI-LRMS (HP 5989B).

Sample	*trans*-Nonachlor pg/g d.w. (ng/g TOC)	*cis*-Nonachlor pg/g d.w. (ng/g TOC)	*trans*-Chlordane pg/g d.w. (ng/g TOC)	*cis*-Chlordane pg/g d.w. (ng/g TOC)	Heptachlor pg/g d.w. (ng/g TOC)
Baltic Sea					
710 (2001)	348 (14)	15 (< 1)	39 (1)	34 (1)	< 8
710 (2002) [a]	n.a.	11 (< 1)	37 (1)	71 (1)	< 8
710 (2004)	119 (25)	2 (<1)	6 (1)	8 (2)	< 8
715 (2001)	137 (4)	18 (< 1)	50 (2)	41 (1)	< 8
715 (2004)	417 (14)	21 (1)	42 (1)	31 (1)	< 8
718 (2001)	198 (7)	21 (< 1)	59 (2)	33 (1)	< 8
718 (2004) [b]	297 (8)	19 (< 1)	47 (2)	41 (1)	< 8
721 (2002) [a]	n.a	21 (< 1)	53 (1)	59 (1)	< 8
721 (2004)	392 (8)	29 (1)	135 (3)	126 (3)	64 (1)
ECKFBU (2004)	444 (11)	19 (< 1)	36 (1)	35 (1)	< 8
ODER (2004)	357 (397)	17 (19)	59 (65)	60 (67)	42 (47)
RUDEN (2004)	334 (12)	6 (< 1)	6 (< 1)	16 (1)	< 8
North Sea					
KS 8 (2002) [a]	n.a.	< 1	2 (1)	7 (2)	< 8
KS 8 (2003)	295 (36)	8 (1)	16 (2)	19 (2)	< 8
KS 8 (2004)	338 (34)	6 (< 1)	21 (2)	18 (2)	< 8
KS 11 (2002) [a]	n.a.	7 (< 1)	39 (2)	84 (5)	< 8
KS 11 (2003)	282 (26)	5 (< 1)	13 (1)	10 (1)	< 8
KS 11 (2004)	[c]	12 (< 1)	27 (1)	35 (1)	< 8
BL 2 (2002) [a]	n.a.	4 (< 1)	8 (1)	13 (2)	< 8
BL 4 (2002) [a]	n.a.	< 1	1 (1)	< 4	< 8
UE 18 (2002) [a]	n.a.	< 1	< 1	< 4	< 8
UE 28 (2002) [a]	n.a.	< 1	< 1	< 4	< 8
ES 1 (2003)	13 (22)	< 1	10 (16)	10 (16)	< 8
Ti 13 (2003)	6 (9)	< 1	10 (14)	8 (11)	< 8
UE 15 (2003)	6 (2)	< 1	25 (11)	10 (4)	< 8
UE 20 (2003)	10 (3)	2 (1)	36 (10)	14 (4)	< 8
L1 (2003)	62 (48)	< 1	5 (4)	< 4	< 8
WB 5 (2003)	28 (6)	< 1	6 (1)	10 (2)	< 8
UE 67 (2003)	7 (6)	< 1	105 (87)	27 (22)	< 8
UE 70 (2003)	7 (10)	< 1	100 (142)	< 4	< 8

[a] no ISTD 4,5-DCCD, quantification of *trans*-nonachlor in both fractions not possible;[b] TOC not available; [c] interferences; n.a. not analyzed

Levels of chlordane isomers detected in this study were in the same range as reported in several publications (see chapter introduction). The mean chlordane concentrations determined in sediments from the Mekong river were ten to twenty times lower than those of PCBs and DDT in sediments (Hung *et al.* 2004). Concentrations of HCHs, HCB, PCBs, DDT group and PAHs found in the North and Baltic Sea are shown in Table 37 (BLMP 2002).

Table 37. Levels of other organic contaminants [ng/g d.w] in sediments form the North and Baltic Sea in 1997/1998 (BLMP 2002).

	North Sea [ng/g d.w]	**Baltic Sea [ng/g d.w]**
HCH	α-HCH: 0.1 (median for KS 11)	α-HCH: < 0.2-1
	γ-HCH: 0.03-0.5	γ-HCH: 0.5-5.9
HCB	< 0.003-0.7	0.09-8.5
PCB (sum of 7)	PCB 153: < 0.01-1.1	1-185
DDT group	p,p' -DDT: < LOD	p,p'-DDT: < 0.01-14.8
	p,p' -DDD: < 0.4-73	p,p'-DDD: <0.2-65.8
		p,p'-DDE: 0.25-26.3
PAH (sum of 6)	147-296	< LOD-1000
Σ Chlordanes (this study)*	**0.03-0.39**	**0.14-0.75**

* Sum of *trans*-chlordane, *cis*-chlordane, *trans*-nonachlor, *cis*-nonachlor and heptachlor

Levels of *cis*-chlordane were higher than those of the *trans* isomer (0.09-0.19 vs. 0.06-0.12 ng/g d.w.) in Baltic Sea sediments (Strandberg *et al.* 1998). Moreover, in most cases the concentrations of *trans*-nonachlor were higher than for *cis*-nonachlor (0.06-0.13 vs. 0.03-0.05 ng/g d.w.). Some authors assumed that the observed distribution of chlordane compounds might come from a diffuse input of these substances in the environment (BLMP 2002).

The concentration ratio of *trans*-nonachlor to *trans*-chlordane can provide information on origin and transport pathways for chlordanes. The technical mixture consists of approximately 24% *trans*-chlordane and 7% *trans*-nonachlor. Ratios higher than 1 can be suggestive for atmospheric input of

chlordanes due to a higher transportability of *trans*-nonachlor which has a higher Henry's law constant than *trans*-chlordane (Iwata *et al.* 1993). Furthermore, *trans*-nonachlor is more persistent and *trans*-chlordane degraded faster. A higher ratio can also be the evidence of an aged chlordane mixture.

Ratios between 2 and 4 were reported for suspended particular matter from the northern part of the Baltic Sea (Strandberg *et al.* 1998). Ratios for sediments were lower. The authors suggested that longe-range air transport of chlordanes from southern latitude countries was the predominant source for those compounds in the Baltic Sea. *trans/cis*-chlordane ratios in sediments from Korea were higher than 1 (Lee *et al.* 2001). This ratio corresponded to that of the technical mixture and indicated the higher persistence of *trans*-chlordane in sediments.

5 CONCLUSIONS AND OUTLOOK

Chloroparaffins were discovered in the environment for the first time nearly thirty years ago. Especially, in the last eight years the analytical methodology was improved considerably and allowed to overcome most of the problems of CP analysis. Complete separation by HRGC-LRMS cannot be achieved due to the high complexity of these mixtures. However, there is a good chance that this aim can be achieved applying multidimensional HRGC techniques. GC×GC results presented in this work showed the separation into at least congener groups and no mass interferences between SCCPs and MCCPs. Therefore, the detection of minor MCCP compounds in the presence of SCCPs is possible. The potential of GC×GC coupled to mass spectrometry should be studied more detailed in the future.

All newly developed mass spectrometric methods were applied as well as a new quantification approach. These low resolution mass spectrometric methods allowed the determination of chloroparaffins in sediments. Their data were comparable to the conventionally applied ECNI-MS and gave results with satisfying accuracy. It could be shown that congener and homologue group patterns obtained by ECNI-MS and CACI-MS were similar after correction. CACI-MS can overcome most of the major problems of the usually applied ECNI method, so higher attention should be paid to this technique. Mass spectrometers containing ion sources with removable ion volumes should be tested for routine analysis.

The first data set of chloroparaffins in sediment from the North and Baltic Sea was generated. Additionally, earlier published concentrations of European rivers were confirmed by studies of sediments and suspended particular matter. However, the consequence of these CP levels cannot be

evaluated, as long as toxicology properties, effect concentrations of CPs and accumulation processes from sediments are insufficiently known. Risk assessment for aquatic organisms is therefore hardly possible.

Chlordane was removed from the market nearly three decades ago due its toxicity. Chlordane and its metabolites or residues are very persistent in the environment, and their presence in sediments still contribute to water pollution. Despite widespread international recognition that chlordane compounds pose a serious health and environmental risk, environmental data are more or less scarce. Especially, little attention has been paid to levels in sediments, although chlordane can enter the food chain through benthic organisms. Furthermore, the consequence of these chlordane levels cannot be evaluated, as long as effect concentrations for aquatic organisms in sediments are not available.

6 REFERENCES

Abadin HG, Baynes R, Goetchius PF (**1994**) Toxicological profile for chlordane. Agency for Toxic Substances and Disease Registry, Atlanta, Georgia, USA, pp. 204.

Alcock RE, Sweetman A, Jones KC (**1999**) *Chemosphere* 38: 2247-2262.

Ballschmiter K, Hackenberg R, Jarman WM, Looser R (**2002**) *Environ. Sci. Pollut. Res.* 9: 274-288.

Barber JL, Sweetman AJ, Thomas GO, Braekevelt E, Stern GA, Jones KC (**2005**) *Environ. Sci. Technol.* 39: 4407-4415.

BLMP (**2002**) Meeresumwelt 1997-1998. Bundesamt für Seeschifffahrt und Hydrographie (BSH), Hamburg, pp. 176.

Borgen AR, Schlabach M, Gundersen H (**2000**) *Organohalogen Compd.* 47: 272-275.

Buchert H, Class T, Ballschmiter K (**1989**) *Fresenius J. Anal. Chem.* 333: 211-217.

Campbell I, McConnell G (**1980**) *Environ. Sci. Technol.* 14: 1209-1214.

Castells P, Santos F J, Galceran MT (**2004**) *Rapid Commun. Mass Spectrom.* 18: 529-536.

Cicero AM, Mecozzi M, Morlino M, Pellegrini D, Veschetti E (**2001**) *Environ. Monit. Assess.* 71: 297-316.

Ciereszko W (**2002**) *Acta Icht. Piscat.* 32: 127-135.

Coelhan M (**1999**) *Anal. Chem.* 71: 4498-4505.

Coelhan M, Saraci M, Parlar H (**2000**) *Chemosphere* 40: 685-689.

Danzer K, Hobert H, Fischbacher C, Jagemann K-U (**2001**) Chemometrik: Grundlagen und Anwendungen. Springer, Berlin, ISBN 3-540-41291-3.

Dearth MA, Hites RA (**1991**) *Environ. Sci. Technol.* 25: 245-254.

Di Toro DM, Zarba CS, Hansen DJ, Berry WJ, Swartz RC, Cowan CE, Pavlou SP, Allen HE, Thomas NA, Paquin PR (**1991**) *Environ. Toxicol. Chem.* 10: 1541-1583.

Drouillard KG, Tomy GT, Muir DCG, Friesen KJ (**1998**) *Environ. Toxicol. Chem.* 17: 1252-1260.

EPA (UK) (**2002**) Pollution Inventory Substances-Chloro-alkanes (C_{14-17}) MCCPs. Available from http://216.31.193.171/asp/1_search_pisubstancehelp.asp?id=1535.

EU (**2002**) Richtlinie 2002/45/EG, Verwendungsverbote für Chlorparaffine, Stand 25.6.2002. EU, Luxemburg, pp. 3.

Eurochlor (**2004**) General Information-Chlorinated Paraffins. Available from www.eurochlor.org.

European Chemicals Bureau (**2000**) European Union Risk Assessment Report for Alkanes, C_{10}-C_{13}, Chloro. Available from http://ecb.jrc.it/existing-chemicals, pp. 134.

European Chemicals Bureau (**2002**) Risk Assessment of Alkanes, C_{14}-C_{17}, Chloro. Draft. Available from http://ecb.jrc.it/existing-chemicals, pp. 317.

European Commission (**1999**) Alkanes, C_{10-13}, Chloro (Short chain length chlorinated paraffins). Joint Research Centre, Institute for Health and Consumer Protection, Ispra, pp. 20.

European Community (**2000**) *Off. J. Eur. Commun.* L327: 1-72.

European Community (**2001**) *Off. J. Eur. Commun.* L331: 1-5.

Farrar DG (**2000**) *Organohalogen Compd.* 47: 129-130.

Fatoki OS, Awofolu RO (**2003**) *J. Chromatogr. A* 983: 225-236.

Fisk AT, Cymbalisty CD, Tomy GT, Muir DCG (**1998**) *Aqua. Toxicol.* 43: 209-221.

Freie und Hansestadt Hamburg (**2000**) Die Elbe und ihre Sedimente. Wirtschaftsbehörde, Strom- und Hafenbau, Hamburg, pp. 6.

Froescheis O, Ballschmiter K (**1998**) *Fresenius J. Anal. Chem.* 361: 784-790.

GDCh Advisory Committee on Existing Chemicals of Environmental Relevance (**1992**) Chlorinated Paraffins. Hirzel, Stuttgart, ISBN 3-7776-0694-6.

Gjos N, Gustavsen KO (**1982**) *Anal. Chem.* 54: 1318-1320.

Government of Canada (**1993**) Priority Substances List Assessment Report - Chlorinated paraffins. Government of Canada, pp. 32.

Greenpeace (**1995**) Chlorparaffine-ein Umweltgift breitet sich aus. Greenpeace, Hamburg, pp. 20.

Gusev MN, Urman YA, Mochalova OA, Kocharyan LA, Slonim IY (**1968**) *Izv. Akad. Nauk SSSR. Khim.* 7: 1549-1552.

Helcom (**2002**) Draft Guidance Document on Short Chained Chlorinated Paraffins (SCCP). European Union, pp. 21.

Hung MN, Kajiwara N, Kunisue T, Subramanian A, Iwata H, Tanabe S, Hung VP, Cach TB (**2004**) *Organohalogen Compd.* 66: 3664-3669.

Hüttig J, Oehme M (**2005**) *J. Environ. Monit.* 7: 319-324.

Iino F, Takasuga T, Senthilkumar K, Nakamura N, Nakanishi J (**2005**) *Environ. Sci. Technol.* 39: 859-866.

Ineos Chlor Limited (**September 2004**) Cereclor™ physical properties data. Available from: http://www.ineoschlor.com, pp. 24.

Iwata H, Tanabe S, Sakai N, Tatsukawa R (**1993**) *Environ. Sci. Technol.* 27: 1080-1098.

Johnson-Logan LR, Broshears RE, Klaine SJ (**1992**) *Environ. Sci. Technol.* 26: 2234-2239.

Junk SA, Meisch H-U (**1993**) *Fresenius J. Anal. Chem.* 347: 361-364.

Karlsson H (**1998**) Isomer and enantiomer selective ultra trace analysis of chlordane in biota including isolation and structure elucidation of single congeners (Thesis). Philosophisch-Naturwissenschaftliche Fakultät. Universität Basel.

Kemmlein S, Hermeneit A, Rotard W (**2002**) *Organohalogen Compd.* 59: 279-282.

Korytar P, Leonards PEG, de Boer J, Brinkmann UAT (**2005a**) *J. Chromatogr. A* 1086: 29-44.

Korytar P, Parera J, Leonards PEG, Sanots FJ, de Boer J, Brinkmann UAT (**2005b**) *J. Chromatogr. A* 1086: 71-82.

Lahaniatis M (**2001**) Quantifizierung von kurz- und mittelkettigen Chlorparaffinrückständen in ausgesuchten fetthaltigen Lebensmitteln (Thesis). Department für Lebensmittel und Ernährung. Technische Universität München.

Lee KT, Tanabe S, Koh CH (**2001**) *Environ. Pollut.* 114: 207-213.

Lehmann M (**2005**) Personal communication.

Lerche D, van de Plassche E, Schwegler A, Balk F (**2002**) *Chemosphere* 47: 617-630.

Lueschow R (**2004**) Personal communication.

Madeley JR, Birtley RDN (**1980**) *Environ. Sci. Technol.* 14: 1215-1221.

Marvin CH, Painter S, Tomy GT, Stern GA, Braekevelt E, Muir DCG (**2003**) *Environ. Sci. Technol.* 37: 4561-4568.

Maulshagen A, Hamm S, Petersen M, Elsholz O, Fengler S, Seel P (**2003**) *Organohalogen Compd.* 62: 371-374.

Moore S, Vromet L, Rondeau B (**2003**) *Chemosphere* 54: 453-459.

Muir DCG, Grift NP, Lockhart WL, Wilkinson P, Billeck BN, Brunskill GJ (**1995**) *Sci. Total Environ.* 160/161: 447-457.

Muir DCG, Norstrom RJ, Simon M (**1988**) *Environ. Sci. Technol.* 22: 1071-1079.

Muir DCG, Stern GA, Tomy GT (**2000**) Chlorinated paraffins. The Handbook of Environmental Chemistry. Springer Verlag, Berlin, Vol 3. ISBN 3-540-65338-6.

Nicholls CR, Allchin CR, Law RJ (**2001**) *Environ. Pollut.* 114: 415-430.

Oehme M (**1991**) *Sci. Total Environ.* 106: 43-53.

Oehme M (**1998**) Practical Introduction to GC-MS Analysis with Quadrupoles. Hüthig, Heidelberg, ISBN 3-7785-2602-2.

Offenberg JH, Nelson ED, Gigliotto CL, Eisenreich SJ (**2004**) *Environ. Sci. Technol.* 38: 3488-3497.

Omori T, Kimura T, Kodama T (**1987**) *Appl. Environm. Microbiol.* 25: 553-557.

Panzel H, Ballschmiter K (**1974**) *Fresenius J. Anal. Chem.* 271: 182-191.

Parera J, Santos FJ, Galceran MT (**2002**) *Organohalogen Compd.* 55: 195-198.

Parera J, Santos FJ, Galceran MT (**2004**) *J. Chromatogr. A* 1046: 19-26.

Peters AJ, Tomy GT, Stern GA, Jones KC (**1998**) *Organohalogen Compd.* 35: 439-442.

Peters JP, Tomy GT, Jones KC, Coleman P, Stern GA (**2000**) *Atmos. Environ.* 34: 3085-3090.

Pribylova P, Klanova J, Holoubek I, Coelhan M (**2005**) *Organohalogen Compd.* 67: 1330-1333.

Pyle SM, Marcus AB (**1997**) *J. Mass Spectrom.* 32: 897-898.

Reth M, Oehme M (**2004**) *Anal. Bioanal. Chem.* 378: 1741-1747.

Reth M, Zencak Z, Oehme M (**2005a**) *Chemosphere* 58: 847-854.

Reth M, Zencak Z, Oehme M (**2005b**) *J. Chromatogr. A* 1081: 225-231.

Rostad CE (**1997**) *Arch. Environ. Contam. Toxicol.* 33: 369-377.

Schmid PP, Müller MD (**1985**) *J. Assoc. Off. Anal. Chem.* 68: 427-430.

Shojania S (**1999**) *Chemosphere* 38: 2125-2141.

Simpson CD, Wilkins AL, Langdon AG, Wilcock RJ (**1996**) *Mar. Pollut. Bull.* 32: 499-503.

Stejnarova P, Coelhan M, Kostrhounova R, Parlar H, Holoubek I (**2005**) *Chemosphere* 58: 253-262.

Stern GA, Tomy GT (**2000**) *Organohalogen Compd.* 47: 135-138.

Stevens JL, Northcott Gl, Stern GA, Tomy GT, Jones KC (**2003**) *Environ. Sci. Technol.* 37: 462-467.

Strandberg B, Van Bavel B, Bergqvist P-A, Broman D, Ishaq R, Näf C, Pettersen H, Rappe C (**1998**) *Environ. Sci. Technol.* 32: 1754-1759.

Sunito LR, Shiu WY, Mackay D, Seiber JN, Glotfelty D (**1988**) *Rev. Environ. Contam. Toxicol.* 103: 1-59.

Thompson R, Comber M (**2000**) *Organohalogen Compd.* 47: 139-140.

Tomy GT, Fisk AT, Westmore JB, Muir DCG (**1998a**) *Rev. Environ. Contam. Toxicol.* 158: 53-128.

Tomy GT, Muir DCG, Stern GA, Westmore JB (**2000**) *Environ. Sci. Technol.* 34: 1615-1619.

Tomy GT, Stern GA (**1999**) *Anal. Chem.* 71: 4860-4865.

Tomy GT, Stern GA, Lockhart WL, Muir DCG (**1999a**) *Environ. Sci. Technol.* 33: 2858-2863.

Tomy GT, Stern GA, Muir DCG, Fisk AT, Cymbalisty CD, Westmore JB (**1997**) *Anal. Chem.* 69: 2762-2771.

Tomy GT, Tittlemier SA, Stern GA, Muir DCG, Westmore JB (**1998b**) *Chemosphere* 37: 1395-1410.

Tomy GT, Westmore JB, Stern GA, Muir DCG, Fisk AT (**1999b**) *Anal. Chem.* 71: 446-451.

Umweltbundesamt (**2003**) *Umwelt* 2: 120.

UNECE ad hoc Expert Group on POPs (**2003**) Short Chain Chlorinated Paraffins (SCCP) - Substance Dossier, Final Draft II. UNECE, pp. 134.

van Metre P, Callender E, Fuller CC (**1997**) *Environ. Sci. Technol.* 31: 2339-2344.

World Health Organization (**1984**) Environmental Health Criteria 34 - Chlordane. WHO, Genf, ISBN 92-4-154-094-x.

World Health Organization (**1996**) Environmental Health Criteria 181-Chlorinated Paraffins. WHO, Genf, ISBN 92-4-157-181-0.

WWF (**2005**) Clean Baltic within reach? Available from www.panda.org/detox, pp. 39.

Zencak Z (**2004**) Specific alternative mass spectrometric techniques for the trace analysis of chlordanes and polychlorinated *n*-alkanes (Thesis). Philosophisch-Naturwissenschaftliche Fakultät. Universität Basel.

Zencak Z, Borgen A, Reth M, Oehme M (**2005**) *J. Chromatogr. A* 1067: 295-301.

Zencak Z, Oehme M (**2004**) *Rapid Commun. Mass Spectrom.* 18: 2235-2240.

Zencak Z, Oehme M, Skopp S (**2001**) *Rapid Commun. Mass Spectrom.* 15: 1719-1725.

Zencak Z, Reth M, Oehme M (**2003**) *Anal. Chem.* 75: 2487-2492.

Zencak Z, Reth M, Oehme M (**2004**) *Anal. Chem.* 76: 1957-1962.

Zitko V (**1973**) *J. Chromatogr.* 81: 152-155.

Zitko V (**1980**) The Handbook of Environmental Chemistry, Part A: Anthropogenic Compounds. Springer Verlag, Heidelberg, ISBN 35-40515-992.

EIDESSTATTLICHE ERKLÄRUNG

Ich erkläre, dass ich die Dissertation „**Determination of the "new" problem group chloroparaffins in sediments by HRGC-LRMS**“ nur mit der darin angegebenen Hilfe verfasst und bei keiner anderen Universität und bei keiner anderen Fakultät der Universität Basel eingereicht habe.

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